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Microstructure and creep strength of different γ/γ'- strengthened Co-base superalloy variants

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Keywords: superalloy, cobalt, thermal stability, volume fraction, creep

Abstract

The influence of W, Ta, Ti, Nb, V, Si, Mo, Ir and Cr on the high temperature properties of γ/γ′-strengthened Co-Al-W superalloys was investigated. All alloys exhibit a γ/γ′-microstructure with remarkably differing γ′-volume fractions. W, Ta, Ti, Nb, V increase the γ′-volume fraction and γ′-solvus temperature. An increased W content and alloying of additional elements except of Ir decreased the liquidus temperature. First creep experiments revealed creep strength comparable to polycrystalline Ni-base superalloys and importance of the grain boundary strengthening.

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The influence of W, Ta, Ti, Nb, V, Si, Mo, Ir and Cr on the high temperature properties of gamma/gammaprime-strengthened Co-Al-W superalloys was investigated. All alloys exhibit a gamma/gammaprime-microstructure with remarkably differing gammaprime-volume fractions. W, Ta, Ti, Nb, V increase the gammaprime-volume fraction and gammaprime-solvus temperature. An increased W content and alloying of additional elements except of Ir decreased the liquidus temperature. First creep experiments revealed creep strength comparable to polycrystalline Ni-base superalloys and importance of the grain boundary strengthening.

Conventional Co-base superalloys are suitable materials for use in a corrosive environment at high temperatures like in a gas turbine. However, the high temperature strength of these classic Co-superalloys alloys can not compete with the excellent high temperature properties of γ/γ′-strengthened Ni-base superalloys [1]. Recently a ternary compound $Co_3(Al,W)$ with the $L1_2$ structure was discovered by Sato et al [2]. This led to the development of a new class of high temperature Co-base superalloys with a γ/γ′-microstructure similar to Ni-base superalloys [3, 4]. Further investigations by Suzuki et al. [5, 6] revealed the occurrence of a flow stress anomaly similar to Ni-base superalloys. The flow stress at the peak temperature increases by addition of Ta. Moreover, it was found that Ta stabilizes the γ′-phase and increases the γ′-solvus temperature. Shinagawa et al. [7] showed that boron enhances the ductility of the Co-9Al-9W (at.%) system by strengthening the grain boundaries. Ab-initio calculations [8] confirmed experimental results [9] that the $L1_2$ $Co_3(Al,W)$ compound is ductile in nature and can be used as a hardening phase.

In this study several polycrystalline γ′-hardened Co-base superalloys containing additional elements were investigated by means of differential scanning calorimetry and scanning electron microscopy. Mechanical properties were examined by the first creep experiments on this new alloy class in compression. In the present paper the influence of alloying elements on the evaluated properties is discussed.

The composition of the alloys under investigation and the abbreviations used to name the alloys subsequently are given in Table 1. The alloy selection was made with the aim to investigate the influence of various alloying elements on the thermophysical properties of the alloy system like γ′-solvus temperature, γ′-volume fraction, γ/γ′-microstructure and on the creep resistance. The W-content was reduced to decrease the density and to check whether the other elements can substitute W in the $L1_2$ phase thus leading to an extra reduction in density.

The experimental alloys were vacuum arc melted as 100 g ingots, solution heat treated at 1300 °C for 12 hours in argon atmosphere and aged at 900 °C for 200 hours in air. Due to the high melting point of W and the evaporation of Al during the arc melting the compositions of the experimental alloys differ slightly from the nominal compositions. The concentrations of the alloying elements as measured by EDX on solution heat treated samples, are given in Table 1. For quantitative results a quantitative optimization using a Co standard was performed prior to each measurement. This is still less accurate than a proper wet chemical

analysis but adequate for the present purpose and for comparison with similar EDX studies in literature .

Table 1: Investigated alloys, utilized abbreviations and measured compositions.

Utilized abbreviations	Nominal composition	Measured composition / at. %				
		Co	Al	W	Ta	X
9W	Co-9Al-9W	83.4	8.1	8.4	-	-
10W2Nb	Co-9Al-10W-2Nb	78.6	9.4	10.2	-	1.8
10W2Ti	Co-9Al-10W-2Ti	79.1	8.4	10.3	-	2.2
10W2V	Co-9Al-10W-2V	77.5	9.0	11.4	-	2.1
10W2Ta	Co-9Al-10W-2Ta	81.6	7.6	9.2	1.9	-
9W0.1B	Co-9Al-9W-0.1B	82.2	8.3	9.4	-	-
8W2Ta	Co-9Al-8W-2Ta	81.5	8.1	8.4	2.0	-
2Ta2Cr	Co-9Al-8W-2Ta-2Cr	81.4	8.0	7.2	1.6	1.9
2Ta2Nb	Co-9Al-8W-2Ta-2Nb	82.6	8.0	6.7	1.4	1.4
2Ta2Si	Co-9Al-8W-2Ta-2Si	81.2	8.1	7.7	1.6	1.8
2Ta2V	Co-9Al-8W-2Ta-2V	80.4	8.2	7.5	1.9	2.0
2Ta2Mo	Co-9Al-8W-2Ta-2Mo	78.5	8.2	9.6	1.8	1.8
2Ta2Ir	Co-9Al-8W-2Ta-2Ir	78.6	8.1	9.1	1.7	2.5
5W2Ta2Mo	Co-9Al-5,5W-2Ta-2Mo	82.8	8.0	5.7	2.0	1.5
5W2Ta2Ir	Co-9Al-5,5W-2Ta-2Ir	83.5	8.7	5.5	1.3	0.9

Differential scanning calorimetry analysis (DSC) was conducted on cuboidal specimens with a mass of about 300 mg with a heating/cooling rate of 5 K/min using a Netzsch STA 409 CD at the Institute of Science and Technology of Metals, University of Erlangen.

Microstructure characterization of the alloys was carried out in a Zeiss Crossbeam 1540 EsB with an Oxford Instruments EDS system. The samples were polished and subsequently etched with Spar etchant solution (100ml distilled water, 100ml HCl (32%), 10ml HNO_3 (65%) and 0.3ml Spar-etchant with 1-metoxy-2-propanol as the main constituent).

Creep experiments in compression mode were performed at 850 °C in air at a constant applied stress. Creep samples were produced by electro-discharge machining. The specimens have a cylindrical geometry with a height of 7.5mm and a diameter of 5mm. The creep tests were performed up to a maximum plastic strain of less than 5%.

In order to determine the phase stability of the experimental alloys DSC measurements were performed in as cast condition.

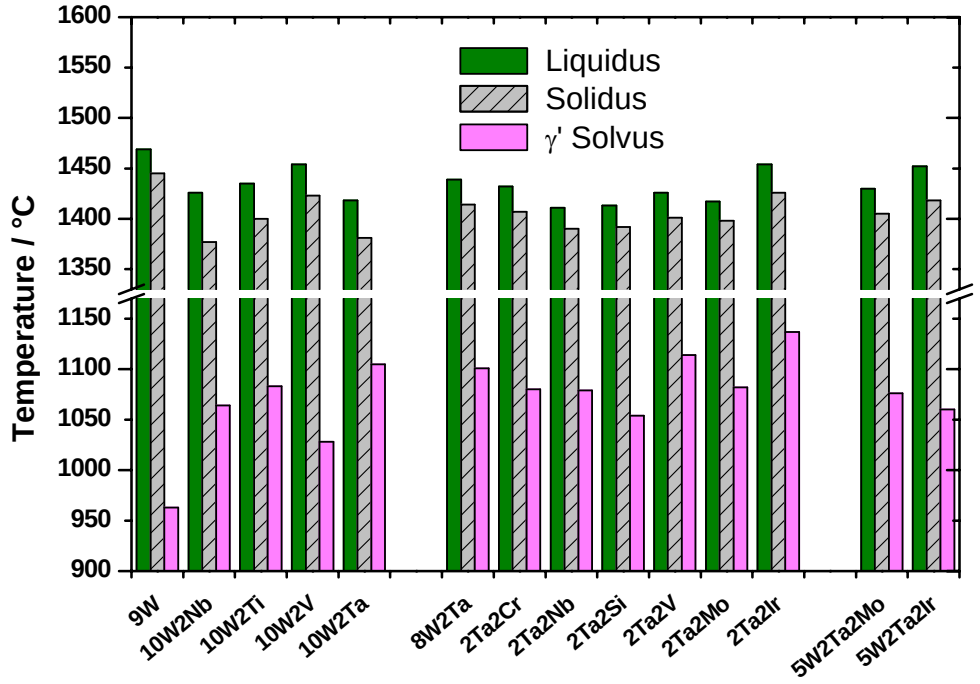

Figure 1: DSC data of the investigated alloys.

The results of the DSC measurements in Figure 1 show that the 9W alloy has the highest liquidus temperature T_{liquid} of 1469 °C of all studied alloys. Addition of further elements to the Co-9Al-10W system as well as to the Co-9Al-8W-2Ta system decreases T_{liquid} of the alloys. The addition of 2 at.% Ta to the 9W alloy decreases T_{liquid} to 1439 °C. An additional increase in the tungsten content in this alloy decreases the T_{liquid} even more. Both values are in a good agreement with the results published by Sato et al. and Suzuki et al. [2, 5]. The only exception is the Ir-containing alloy. The liquidus temperature increases in this case by about 15°C. The higher melting temperature of Ir in the binary Co-Ir system exhibiting complete solid solubility can be the reason for this. The reduced tungsten content in the Ir containing quinary alloy 5W2Ta2Ir had almost no influence on the T_{liquid}. The Mo containing counterpart 5W2Ta2Mo exhibited a 13 K increased T_{liquid} with decreasing tungsten content. Such behavior is also reported by Suzuki et al. in the Co-Al-W system [6]. A temperature of 1300 °C for the solution heat treatment was chosen since the solidification range is above this temperature.

The γ′-precipitation temperatures are discussed based on the DSC cooling data since the solvus temperature of the γ′- phase could be determined more accurately than based on

heating data. However, it should be considered, that values on heating would have been slightly higher.

In contrast to the liquidus temperature, where the 9W alloy exhibits the highest value, the γ′-solvus temperature in the 9W alloy has the lowest value of 963 °C. Addition of 2 at.% Ta, Ti, Nb or V to the Co-Al-W system significantly increases T_{solvus}. For Ta and Nb such a trend was reported earlier by Sato et al. [2]. However, further alloying of the quaternary system with Si, Mo or Cr led to a decreased T_{solvus}. Cr is known to stabilize the fcc matrix [2]. The decreasing effect of Si and Mo on the γ′-solvus temperature has not been reported yet.

In contrast to the results of Suzuki et al. [6] in the ternary alloys, an increased W content in the quaternary alloys led to a minor increase in the T_{solvus}. Addition of V or Ir to 8W2Ta alloy increased T_{solvus}, with the Ir containing alloy exhibiting the highest value of investigated alloys possibly due to the formation of $(Co,Ir)_3(Al,W)$ [2]. The variant with the reduced tungsten content 5W2Ta2Ir shows a reduced T_{solvus} by about 77K and can be explained by the simultaneously lowered Ta and Ir content due to insufficient melting in this alloy. The reduction in the Mo containing counterpart is only 6K. Thus it can be assumed that tungsten does not have an significant impact on the T_{solvus} of the γ′-phase as confirmed by a similar T_{solvus} in 8W2Ta and 10W2Ta. Therefore, among the investigated elements only Ir has an advantageous influence on both T_{solvus} and the T_{liquid} of the Co-Al-W-Ta system. A temperature of 900°C was chosen for aging since the γ′-precipitation range of all investigated alloys is above this temperature.

Considering the γ′-solvus temperatures and the solvus temperatures of the alloys there is a heat-treatment window of at least 200 degrees. Therefore, the alloys presented in this work are suitable materials for application as wrought alloys.

Micrographs of the aged alloys are presented in Figure 2 and show the two phase γ/γ′-microstructure which has been obtained for all alloy variants. The microstructures of the alloy 9W as well as the 10W2Ta are similar to the results published earlier by Sato et al. and Suzuki et al. [2, 5]. The values for the size of the γ′-precipitates among the alloys do not show significant variation except for some alloys exhibiting coarsening and therefore will not be discussed further. However, the values of the γ′-volume fraction show remarkable variation (Figure 2 and 3) and therefore have been determined quantitatively by binarizing an SEM image and calculating the area fraction utilizing ImageJ software. The analyzed area was about 3.8 µm x 2.6 µm.

The reason for the variation in the γ′-volume fraction is not only the distribution of the alloying elements between the γ- and γ′-phase, but also the possible substitution of the elements in the $L1_2$ γ′-Co_3(Al,W) compound, having three nonequivalent Co sites at the face centers and Al and W sites at the cube corners as reported by Chen et al. [10]. Thus, only elements which distribute to the γ′-phase and occupy Al or W sites (like Ta or Mo [10]) at the Co_3(Al,W) compound should lead to an increasing γ′-volume fraction since these are the limiting elements for the formation of the γ′-phase. Indeed, the additions of 2 at. % of Ta, as well as Nb, Ti and V to the ternary alloy show a substantial increase in the γ′-volume fraction from 58 % to about 82%. Thus these elements have a definite stabilizing effect on the γ′-phase, since they also increase the γ′-solvus temperature. The extra addition of W to the 8W2Ta led to a further increase in the γ′-volume fraction in the alloy 10W2Ta. The effect of W will be discussed in more detail later. Both, the effect of Ta and W on the γ′-volume fraction has also been reported earlier by Sato et al. and Suzuki et al. [2, 5].

The additions of Cr, Nb, Si, V, Mo and Ir to the quaternary alloy 8W2Ta have a highly diverse influence on the γ′-volume fraction. In case of Ir the value does not change. This is in good agreement with results of Chen et al. predicting Ir to occupy Co sites in the Co_3(Al,W) compound. However, Ir slows down the diffusion processes in the alloy since the size of the γ′-precipitates is relatively small. Addition of Si leads to a strongly decreased γ′-volume fraction. Possibly Si tends to distribute to the γ-matrix and therefore destabilizes the γ′-phase. DSC data confirms this. So far the influence of Si has not been studied before. Addition of Cr led to a slightly decreased γ′-volume fraction. As reported by Sato et al. [2] Cr tends to distribute to the γ-phase. A further reason for the decrease is the lowered W content in the 2Ta2Cr alloy compared to the quaternary alloy (Table 1).

The positive effect of V on the γ′- volume fraction can be seen in the alloys 10W2V and 2Ta2V as well. Addition of V lead to a significant increase in the γ′-volume fraction suggesting the behavior of V being similar to that of Ta. Since the density of V is very low, this element can be used in terms of density reduction of the alloy system as reported recently by Pollock et al. [11]. The effect of Nb additions was expected to be similar to V. However, addition to the quaternary alloy led to a slightly decreased γ′-volume fraction. This is supposed to be due to a lowered W content similar to the Cr-containing alloy. Although the W content is lower than in the 2Ta2Cr, the γ′-volume fraction is slightly increased. The addition of Nb to the ternary alloy also shows the stabilizing effect of Nb on the γ′-phase. Results in literature confirm this statement [2]. Mo has a high impact on the γ′-volume fraction. The

alloy 2Ta2Mo exhibits the highest value of 91% γ′ and supports the result of Chen et.al. [10] predicting Mo to occupy the W sites in the $Co_3(Al,W)$ compound. Thus Mo is a further possible candidate for the replacement of W in order to decrease the density. The effect of W on the γ′-volume fraction has also been observed on two additional alloy pairs. The lowered W content in the quinary alloys containing Mo and Ir shows in both cases a significantly decreased γ′-volume fraction. The effect of Mo is obvious in this comparison, since the γ′-volume fraction in the 5W2Mo is still high enough to exhibit a γ/γ′-microstructure comparable with conventionally used Ni-based superalloys. Thus Ta and Mo can substitute a reduced W content. In the 5W2Ir alloy only Ta is left to replace W in the $L1_2$ compound, thus the γ′-volume fraction is comparable to that of the ternary alloy.

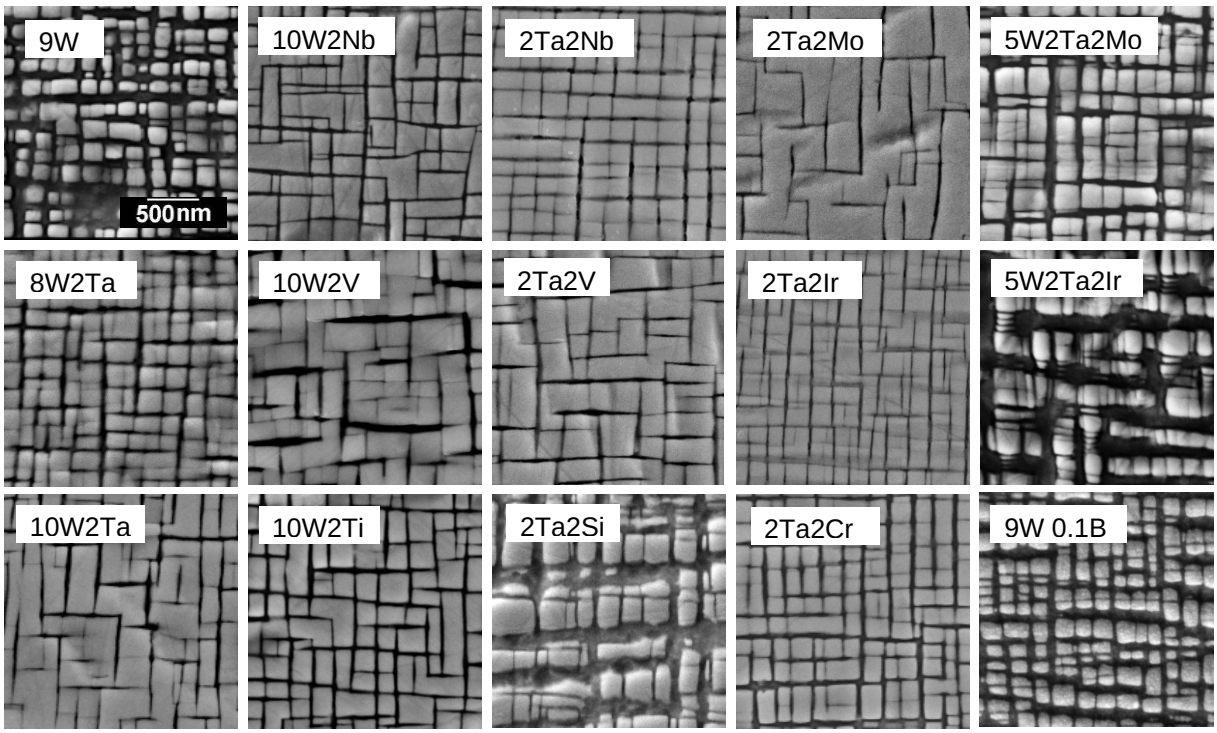

Figure 2: SEM micrographs of the investigated alloys.

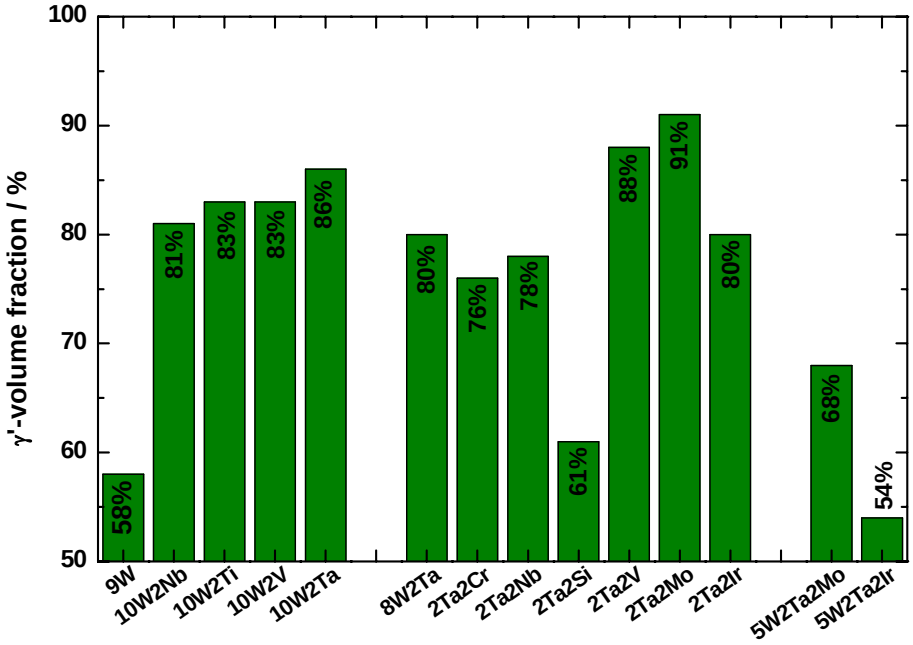

Figure 3: Volume fractions of the γ′-phase of the investigated alloys.

First creep tests were performed on some of the samples described here. However, it became clear during creep testing that it is necessary to strengthen the grain boundaries in these polycrystals otherwise the samples fail by decohesion of the grain boundaries, resulting in a very low creep strength. Therefore, only results of a boron modified alloy are presented here. In this alloy precipitates form at the grain boundary (Figure 4b) after the same heat treatment procedure as of all other alloys. Since EDX measurements have evidenced a local increase of the tungsten content, they are likely to be tungsten borides. These precipitates presumably account for the increased grain boundary strength. However, they were not found in the boron-containing Co-Al-W alloys reported by Shiganawa et al. [7] possibly due to the lower boron content.

Even though there is a certain γ′-depleted region near the grain boundary, the results of the creep experiments on this alloy (Figure 4a) demonstrate that the B-containing ternary alloy has similar creep properties as the commercially available Ni-base superalloy IN713C. In the creep experiments at 350 MPa and 450 MPa a clear minimum in the creep rate was reached at about 0,6% – 0,8% plastic strain. At 250 MPa however, no minimum has been reached in the test. The data point at 250 MPa therefore only gives an upper limit for the minimum creep rate. Results on further creep experiments will be reported soon.

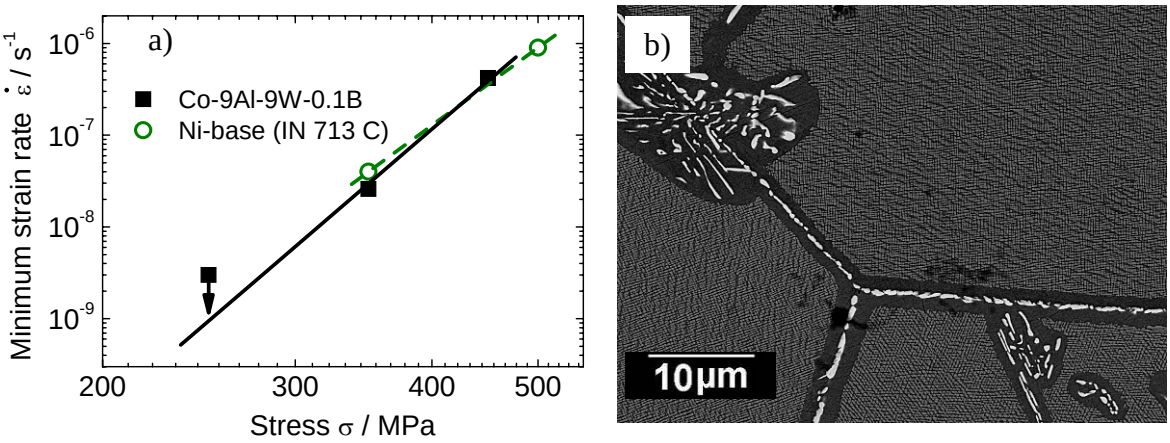

Figure 4: A) Norton Plot of the creep experiments. B) Microstructure of the alloy 9W 0.1B.

Several Co-base alloy variants have been investigated which show a clear γ/γ′-microstructure. The γ′-volume fraction varies from 50% to over 90%. Alloying of additional elements as well as an increased W content lead to a decreased liquidus temperature of the alloys. Only Ir increases the liquidus temperature. Addition of Ta, Ti, Nb and V stabilizes the γ′ phase by increasing its solvus temperature as well as its volume fraction. The grain boundary strength plays a key role for the mechanical properties. Boron containing alloy exhibits precipitates at the grain boundaries leading to good creep properties. Here the first creep tests on this new alloy class are presented, which show that the creep rate is comparable with commercial polycrystalline Ni-base superalloys. Further optimization of γ/γ′-strengthened Co-base superalloys probably will allow to reduce the creep rate even more. Therefore this new superalloy class seems to be very attractive for future application as new high temperature materials.

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