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Thermal stability of γ′ phase in long-term aged Co-Al-W alloys

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ABSTRACT

Three cast alloys with compositions of Co-9Al-8W-0.1B, Co-9Al-9W-0.1B and Co-9Al-11W-0.1B (all atomic percent) were aged at 900 °C for 200 h, 500 h, 1000 h, 2000 h, 5000 h and 10000 h to investigate the thermal stability of $L1_2$ type γ′-Co_3(Al,W) precipitates. The microstructure during the extended ageing process was observed by Scanning and Transmission Electron Microscopy in order to investigate the evolution of the γ/γ′ two-phase microstructure and the formation of any additional phases. It was found after 5000 h ageing that four phases, γ, γ′, $D0_{19}$ and B2, were present within the microstructure as identified by X-ray Diffraction combined with Transmission Electron Microscopy and Electron Back-scattered Diffraction. The γ′ precipitates coarsened according to modified Lifshitz, Slyozov and Wagner theory generally. The fraction of γ′ phase decreased while that of $D0_{19}$ phase increased contrarily. The phase transformation process from γ′-$L1_2$ to $D0_{19}$ was illustrated by Transmission Electron Microscopy. Stacking faults were identified as the initial step of the decomposition of the γ′ phase.

1. Introduction

The discovery of a new type of Co-base superalloys strengthened by a ternary Co_3(Al,W) compound with an $L1_2$ ordered structure (γ′ phase) was reported by Sato et al., in 2006 [1]. Ni-base superalloys with a similar aligned coherent γ/γ′ two-phase microstructure are widely known for their excellent high temperature mechanical properties [2]. Prior to the discovery of Sato et al. [1], such hardening effects by γ′ phase precipitation were unknown in Co-base superalloys and thus such alloys had a worse high-temperature capability compared to Ni-base superalloys [3]. The discovery of such novel types of Co-base superalloys, which can exhibit a high volume fraction of coherently embedded γ′ phase with a solvus up to 1000 °C, offers the possibility of developing similar or even superior mechanical properties compared to the γ′ hardened Ni-base superalloys. Taking into account that the melting point of cobalt is slightly higher than that of nickel, the prospects of attaining better high temperature capability are promising [3–11].

Unfortunately, there is a high degree of uncertainty about the stability of the γ′ phase in these novel Co-base superalloys. Some authors report it to be metastable at 1000 °C but stable at 900 °C [1,3–8,12]. However, Kobayashi and Lass et al. [13,14] reported that the γ′ precipitates are also metastable at 900 °C and decompose into the hexagonal $D0_{19}$ phase over time. According to most literature sources [3,9,13–18], no stable γ/γ′ two-phase region exists in the ternary Co-Al-W system, but the γ matrix phase is in thermodynamic equilibrium with the CoAl (B2) and Co_3W ($D0_{19}$) phase at 900 °C.

Therefore, to acquire the necessary knowledge to develop this material class into alloys suited for application, it is of high interest to characterize and understand the long-term stability of the γ/γ′ structure and the mechanisms operating during the transformation of the γ′-Co_3(Al,W) phase into other phases. In order to achieve this, a number of ternary Co-Al-W alloys with W contents between 8 and 11 at.% were heat treated for up to 10000 h and the changes in microstructure, including γ′ fraction and particle size, as well as the formation of other phases was investigated. In particular the details of the transformation from γ′ phase to $D0_{19}$ phase during long-term ageing at 900 °C were investigated.

2. Experimental procedure

2.1. Sample preparation

The alloys investigated were Co-9Al-8W-0.1B, Co-9Al-9W-0.1B

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and Co-9Al-11W-0.1B (all atomic percent in nominal composition), and had been produced by argon arc melting. For the sake of brevity, in the following these alloys will be termed as 8W, 9W and 11W respectively. The ingots were melted from their elements and then remelted 5 times into 64 g buttons to achieve chemical homogeneity. A small amount of boron was added to the alloys to strengthen the grain boundaries and suppress grain boundary fracture. This was done to investigate alloy compositions which could in modified form be suited as polycrystalline material for industrial applications [19] and to ensure that the polycrystalline specimens were suited for mechanical testing without premature failure at grain boundaries [20]. For comparison purposes by the same method a boron free specimen with the composition Co-9Al-9W was also produced.

2.2. Heat-treatment

Solution heat-treatment was conducted at 1300 °C for 12 h in a vacuum furnace. Subsequent ageing treatments were performed at 900 °C in air for times of 200 h, 500 h, 1000 h, 2000 h, 5000 h and 10000 h. After ageing the specimens were air cooled. The solution and ageing treatment temperature employed was based on the melting points and γ′ solvus temperatures reported in Ref. [18].

2.3. Microstructure characterization

The specimens for microstructural characterization by scanning electron microscopy (SEM) were prepared by grinding, polishing, and then electro-polishing for 90 s in a solution of 2-buthanol and perchloric acid in methanol at −41 °C with a voltage of 25 V. Backscattered Electron (BSE) images as well as Electron Backscattered Diffraction (EBSD) maps were obtained using a Leo Gemini 1530 and a Zeiss Auriga SEM both equipped with field emission electron guns and TSL EBSD analysis systems. The transmission electron microscope (TEM) specimens were cut and ground to about 60 μm thickness and subsequently electrolytically thinned to electron transparency using the Struers A3 electrolyte with a voltage of 20 V at −38 °C. They were investigated using a Philips CM200 TEM operated at 200 kV. X-ray diffraction (XRD) measurements were carried out to identify the phases in the specimens. Room temperature XRD was conducted using a Siemens D5000 diffractometer at 40 kV and 40 mA, the wavelength of the X-rays corresponded to copper Kα (1.5418 Å). Additional diffraction measurements were performed at the synchrotron radiation beamline HEMS run by Helmholtz-Zentrum Geesthacht at PETRA III of the Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany. The specimens had a 5 mm diameter and were measured in transmission with a beam size of 1 mm × 1 mm and an X-ray energy of 100 keV (λ = 0.1240 Å).

The area fraction of $D0_{19}$ phase was determined from the SEM micrographs using the software ImageJ with the threshold-based segmentation method. The area of B2 phase was ignored because of its extremely small amount and its distribution around $D0_{19}$ needles or at grain boundaries. The area fraction and particle size of the γ′ precipitates were determined using the line segment intersection method in Photoshop. For every specimen at least 400 precipitates in 4 different areas within the γ/γ′ regions with their surface parallel to {001} planes were included in the measurements. To determine the real fraction of γ′ phase the measured area fraction was corrected by excluding the $D0_{19}$ area fraction. As the γ′ particles were cubic and distributed quite evenly, the area fraction directly determined from the micrographs was assumed to be equal to the volume fraction.

3. Results and discussion

3.1. Microstructural evolution

The microstructures of the 8W, 9W and 11W alloys after ageing at 900 °C for times between 200 h and 10000 h are shown in Fig. 1. All micrographs were taken using the SEM backscattering mode. It is clearly visible that even after ageing for 10000 h the microstructure predominantly consists of the γ (Co) matrix with homogeneously distributed cubic γ′ (Co_3(Al,W)) particles as the primary precipitate phase in the matrix. Additional phases appearing brighter in the images are also present, which seem to increase in fraction and size in all three alloys with increasing ageing time.

To identify the type of these additional phases, XRD and analysis of selected area diffraction pattern (SADP) in TEM were employed. Fig. 2a–c) shows the XRD patterns of the three boron containing alloys after ageing for 200 h and 2000 h as well as the HEXRD pattern of the alloy Co-9Al-9W after ageing for 5000 h shown in Fig. 2d. The positions where diffraction peaks are expected for the phases γ′, $D0_{19}$ and B2 are indicated. The majority of the diffraction peaks from the γ phase overlap with those of γ′ phase due to their similar crystal structure and lattice constants. Thus, γ phase peaks are not separately marked in Fig. 2. In addition to the desired γ/γ′ phases, a $D0_{19}$ phase is present in 8W and 9W already in a specimen state which can be considered as kind of standard heat-treated (200 h). Only one small $D0_{19}$ peak is found in 11W after ageing for 200 h which probably corresponds to the bright particles visible in Fig. 1c1. The reason why only one weak peak of this phase is detected may be due to its very low volume fraction or an unsuitable orientation of the phase to satisfy the diffraction conditions. For all three alloys a number of somewhat stronger $D0_{19}$ peaks are present in the diffractogram after ageing for 2000 h, indicating that the volume fraction of $D0_{19}$ phase increases with ageing time. In addition, small peaks indicating the presence of some B2 phase are found after 2000 h. There are several additional small diffraction peaks not marked at about 39° and 61° in Fig. 2 (2000 h in a, b, c). These can be identified as CoO from a thin oxide layer which grew during the extended ageing of the 2000 h specimens. Based on the SEM and XRD investigations it can be concluded that the γ/γ′ phases exist as the primary phases up to extended ageing times at a typical service temperature of 900 °C. Nevertheless, additional $D0_{19}$ phase is found to have formed after ageing for 200 h and its volume fraction increases after ageing for 2000 h. A very small amount of B2 phase was found in all three alloys after 2000 h ageing. The higher W content seems to delay the formation of the $D0_{19}$-Co_3W phase in the 11W alloy. These findings are in agreement with the results published by Lass et al. [14,21]. In the boron free Co-9Al-9W alloy, peaks corresponding to the phases γ, γ′ and $D0_{19}$ are visible after ageing at 900 °C for 5000 h. B2 is either absent or perhaps its primary (110) diffraction peak was overlapped by the (111) peaks of γ/γ′ phase. Another possible reason is that the amount of B2 phase is below to the detection limit. From the results it can be concluded that the small addition of boron makes no principal difference with respect to phase stability at 900 °C. In the boron free ternary alloy, in addition to the γ and γ′ phases, the $D0_{19}$ phase has also formed after extended ageing at 900 °C.

The results of the XRD investigations have been supplemented by TEM characterization of aged 8W, 9W and 11W alloy specimens. The aim of this was to confirm the XRD results, associate the different phases to the different precipitates morphologies and to find any precipitate phase present with such a low volume fraction or small size that they were not detected by XRD. Fig. 3 shows typical precipitates present in the 8W, 9W and 11W alloys after ageing for 10000 h together with the corresponding SADPs. Most of the precipitates exhibit a needle-shape, but with differing aspect