Quaternary Alloying Effects and the Prospects for a New Generation of Co-base Superalloys

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Abstract

Polycrystalline Co-Al-W alloys with quaternary alloying substitutions have been studied to investigate whether this alloy system might be attractive as an alternative to Ni-base superalloys in high temperature applications. A process route for the alloys was developed and an initial aging heat treatment established. The initial findings indicate that the addition of Ti, Ta and Ni increases the solvus temperature, whereas the addition of Mo lowers it slightly. The addition of Ti, Ta and Ni to the base alloy increased the γ' precipitate size, whereas the addition of Mo had a negligible effect. Diffraction measurements were performed using both X-ray and neutron scattering. Positive lattice misfit values were obtained at both room and elevated temperatures; moreover, the lattice misfit increased with temperature. The thermal expansion coefficient of the γ phase was similar to reference data for Co, whereas the γ' phase had a greater thermal expansion coefficient than the γ phase. Finally, cyclic oxidation experiments have been carried out in air at 800 °C. The CoO scales grown were not protective, and the alloys suffered from spallation during cooling.

Introduction

Recently, the discovery of a new stable L_{12} precipitate, γ' - $\text{Co}_3(\text{Al,W})$, was announced [1] with the prospect that it may form the basis of a new system to compete with Ni-base superalloys. Alloys with a primarily A1 (fcc) Co matrix strengthened by this phase show the flow stress anomaly, with the peak in flow stress occurring around 250 °C below the γ' solvus temperature [2]. It has been shown that $\langle 112 \rangle$ stacking fault ribbons form that can shear the γ' during hot compression testing [2] in a similar manner to that observed in Ni-base superalloys [3, 4]. This

offers the prospect of alloys which are ductile, tough and fatigue resistant. The solidus-solvus heat treatment window of these alloys is greater than 300 °C and the freezing range is less than 45 °C. This enables these materials to be produced by conventional casting and forging routes, even for alloys with γ' fractions in excess of 70 %.

However, a number of issues remain to be addressed before alloys in this class can be considered for application in gas turbine engines. Data on creep resistance is extremely sparse. It has been reported that the addition of grain boundary strengtheners, such as B, is required to suppress grain boundary void formation. With such additions, these alloys exhibit properties similar to IN713C [5]. Some cyclic oxidation measurements of oxide thickness [6] have been presented, but these results can be difficult to interpret due to spallation. At present, it is clear that Co-Al-W ternary alloys alone cannot form a protective alumina scale and that CoO is not protective [7]. Additionally, the fatigue performance is as-yet unknown and some authors believe that the $\text{Co}_3(\text{Al,W})$ phase is metastable, decomposing over time into CoAl and Co_3W [8].

Cobalt alloys are also susceptible to transformation from the A1 to the A3 (hcp) structure, via the propagation of $\langle 112 \rangle$ stacking faults. The presence of these type of dislocations are linked to discontinuous precipitation, where dislocation motion leads to the reconstruction of the γ' microstructure from one composed of ~ 100 nm cubes into alternating lamellae of the A3 and L_{12} phases [9]. Therefore, the microstructural stability of these alloys is likely to be of concern. However, given a stable microstructure, high lattice misfit may be desirable because it gives rise to significant coherency hardening (in addition to order hardening from anti-phase domains). In the limit of a semi-coherent interface, however, high lattice misfit may become undesirable due to the accom-

modation of stresses and/or the generation of dislocations at the matrix-precipitate interface. If present, interface dislocations might give rise to a forest hardening contribution, but consideration of these is more problematic as they may also nucleate mobile dislocations.

In the present paper, we examine the influence of quaternary alloying additions in a Co-7Al-7W (at.%) alloy and their effect on the solvus temperature, density and oxidation behaviour. Diffraction measurements were also performed to obtain the lattice misfit and thermal expansion of the γ and γ' phases using both neutron and synchrotron X-ray diffraction. The prospects for developing a new generation of Co-base superalloys are then discussed.

Experimental Procedures

The nominal compositions of the alloys investigated are given in Table 1. Some hypotheses about the site occupancy of the alloying elements are implied; Ti and Ta have been found to stabilise the γ' phase [1, 10]. However, it has also been suggested that Mo may strengthen the γ matrix phase [11]. In this alloy scheme, it is suggested that Mo and Ta replace W, Ti replaces both Al and W on the (Al,W) sublattice, and Ni substitutes for Co.

50 g finger-shaped polycrystalline ingots were obtained by vacuum arc melting under a back-filled argon atmosphere. A Co-10W (at.%) master alloy was used along with pure elemental pellets of 99.8% Co, 99.9% Al, 99.5% Mo, 99.9% Ti, 99.97% Ni and 99.9% Ta. The as-cast ingots were then solution heat-treated at 1300 °C for 24 h. Subsequently, the ingots were encapsulated in a rectilinear mild steel can with Ti powder packing and super solvus hot rolled at 1150 °C to a sample thickness of ~ 3 mm. The alloys were aged at 80 – 100 °C below the solvus temperature determined using the cooling curve of the differential scanning calorimetry (DSC) thermo-

Table 1: Nominal compositions of the alloys studied and aging conditions employed.

Composition (at.%)	Name	Aging
Co-7Al-7W	Base	765 °C / 200 h
Co-7Al-5W-2Mo	2Mo	715 °C / 200 h
Co-7Al-5W-2Ta	2Ta	900 °C / 100 h
Co-6Al-6W-2Ti	2Ti	790 °C / 200 h
Co-7Al-7W-20Ni	20Ni	790 °C / 200 h

Figure 1: The processing route: (a) the as-cast ingot, (b) the steel can used for rolling, (c) the hot-rolled can and (d) the final ingot (with surface oxide scale) after removal from the can.

gram, Table 1. For all the heat treatments, the alloys were sealed in quartz tubes which were back-filled with argon after evacuation. On completion of the heat treatment, the samples were allowed to cool in the furnace. Figure 1 summarises the processing route.

Alloy compositions were measured using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) at Incotest, Hereford, UK. Density measurements were performed according to ASMT B311-08.

The solvus temperature of the alloys was determined using a Netzsch “Jupiter” simultaneous thermal analysis (DSC/TGA) instrument. Cylindrical specimens 3.5 mm in diameter and 2.5 mm in height were placed in an alumina crucible. An identical alumina crucible was placed onto the reference pan and platinum used as the reference material. The specimen was heated at 10 °C min⁻¹ and cooled at the same rate. All tests were performed under an argon atmosphere.

Microstructural examination was performed using a LEO 1525 field emission gun scanning electron microscope (FEG-SEM) in secondary electron imaging mode. The samples were ground, polished and etched using a Spar etchant solution [5] (100 ml of distilled water, 100 ml of 32 % HCl, 10 ml of 65 % HNO₃ and 0.3 ml of Spar etchant, with 1-methoxy-2-propanol as the main constituent) for 3 s. A JEOL 2000FX transmission electron microscope (TEM) was used to observe the γ/γ' microstructure in the $\langle 100 \rangle$ direction. Specimens were prepared by twin-jet electropolishing using a 5 vol.% solution of perchloric acid in methanol at -30 °C and 18 - 20 V [10]. The samples were magnetic and so FIB-milling (Helios NanoLab-DualBeam) was used to prepare additional small-volume sections for analysis.

Finally, cyclic oxidation experiments were performed on the alloys using $2.5 \times 2.5 \times 2.5$ mm cubes, surface ground to a surface finish of $0.25 \mu\text{m}$ and cleaned and degreased. Flat-bottomed alumina crucibles were used and the samples were tested in air at 800 °C. To contain any spallation products, lids were placed on the crucibles during periodic specimen removal and air cooling, prior to weighing of the crucibles and specimens. The mass change was measured after 4, 16, 36, 64, 100, 144 and 196 h of oxidation.

Synchrotron & Neutron diffraction

The lattice misfit between the γ and γ' phases in Ni-base superalloys is known to have a significant effect on their mechanical properties [12]. Critically, as lattice misfit is known to vary significantly with temperature due to differences in thermal expansion coefficients and elemental partitioning, it is important that the lattice misfit is determined at service temperatures. In alloys with an L1₂ precipitate phase that is coherent with an A1 matrix, the fundamental reflections from each phase commonly overlap. This prohibits unambiguous discrimination of the contribution to these peaks from each phase. Additionally, the superlattice reflections from the L1₂ phase can be weak due to the similarity of the scattering factors from the atoms on each sublattice. In Ni-base superalloys, the superlattice reflections are vanishingly weak. Hence, neutron diffraction is preferred, due to the increased scattering contrast associated with the bound coherent scattering lengths of the elements on each site. To obtain reliable lattice parameter data from both the A1 and L1₂ phases, a combination of synchrotron X-ray and neutron diffraction was used.

Alloys 2Ti and 2Ta were tested in synchrotron X-ray diffraction, whereas 2Mo, 2Ti, 2Ta and 20Ni from the second batch were tested in neutron diffraction. The complementary data obtained using both techniques allowed the contribution of each phase to the diffraction patterns to be calculated with a greater degree of confidence.

Figure 2: (a) Schematic representation of the experimental setup for in-situ synchrotron experiments, figure adapted from Ref [13]. (b) Schematic plan view of the HRPD detector configuration, figure adapted from Ref [14]. (c) Schematic plan view of the Vulcan detector configuration, figure adapted from Ref [15].

For the X-ray synchrotron study, the I12 beamline at the Diamond synchrotron, Didcot, Oxon., UK was used. Hot rolled 3 mm sheet was surface ground and dog-bone specimens were machined with a $19 \times 1.5 \times 2$ mm gauge volume, which was heated using infrared radiation. An 80 keV ($\lambda=0.15675 \text{ \AA}$), $500 \times 500 \mu\text{m}$ monochromated X-ray beam was used and the diffraction data was recorded using a Thales Pixium 2D area detector, 1319 mm from the sample, in

order to obtain full Debye-Scherrer diffraction rings. Samples were heated to just below the γ' solvus temperature and the diffraction pattern recorded with 1 s exposures during isothermal dwells at 50 °C increments in temperature, with the rings integrated to provide intensity- 2θ diffraction spectra using the fit2D software[16].

Neutron diffraction data was acquired using the HRPD beamline at the ISIS facility, Didcot, Oxon., UK. Specimens for this study were hot rolled to a slightly lower reduction than those used in the synchrotron study. Several pieces of each alloy were arranged in a 6 mm vanadium can and placed in a radiant vacuum furnace. HRPD is a high resolution, long flight path time-of-flight (TOF) spallation neutron diffraction beamline with detector banks at 168°, $\pm 90^\circ$ and 30°. For this study, the 168° banks were employed to obtain maximum instrument d-spacing resolution. Typical counting times were 20 min.

Finally, the Vulcan beamline of the Spallation Neutron Source at the Oak Ridge National Laboratory, TN., USA was used to study dog-bone specimens with gauge dimensions of $19 \times 1.5 \times 3$ mm sectioned from the HRPD samples. Vulcan is a medium resolution TOF neutron diffractometer where a gauge volume within the sample can be heated using electromagnetic induction and subjected to a mechanical load, in this instrument detectors are located at $\pm 90^\circ$.

Si powder standards were used to calibrate all the instruments. The intensity- 2θ profiles and the intensity-TOF profiles were fitted using Rietveld refinement with the General Structure Analysis System (GSAS) [17] program to obtain the lattice parameters of each phase and estimate the weight fractions of each phase. The three setups are depicted in Figure 2.

Results

The actual compositions achieved, the γ' solvus temperatures and the densities of all the alloys are given in Table 2. For the first batch of alloys, the desired compositions were achieved within 0.3 at.%, except for Al, where compensating for evaporation during melting is problematic. Examining the data, substitution of 2Mo for W lowers the γ' solvus temperature markedly, suggesting that it is a γ -stabiliser. In agreement with other studies where 2Ta was added [2, 5], the substitution of 2Ta for W increased the solvus temperature by 138 °C, while the substitution

Table 2: Actual compositions, solvus temperatures and densities, ρ , of the alloys. The neutron diffraction data was obtained from alloys from a second batch (“#2”); the micrographs and cyclic oxidation data are from the first batch prepared. For the second batch of alloys, compositions were obtained by wide-area EDX in the SEM. The γ' area fractions A_f are also provided.

Alloy	Composition at.%			Solvus °C	ρ g cm ⁻³	A_f %
	Al	W	others			
Base	7.3	6.8		854	9.18	61
2Mo	7.2	4.7	1.8 Mo	804	8.92	64
2Ta	9.9	4.8	1.8 Ta	992	9.09	42*
2Ta#2	8.4	4.7	1.7 Ta	982	—	—
2Ti	6.3	6.0	2.2 Ti	919	9.16	58
2Ti#2	5.2	5.3	2.0 Ti	921	—	—
20Ni	7.3	7.0	20.2 Ni	881	9.29	50
20Ni#2	6.3	6.4	18.1 Ni	902	—	—

of 2Ti for 1Al-1W also increased the solvus by 65 °C. Surprisingly, substitution of Ta (rather than the addition of Ta performed in other studies) decreased the γ' content, although there is a hint in the SEM micrographs that a substantial additional fraction of tertiary γ' may be present. The substitution of 20Ni for Co raised the solvus by 27 °C, in contrast with the results of Ooshima *et al.* [18] who found that a 2Ni addition decreased the γ' solvus and the γ' content by small amounts. However, it was found that 20Ni substitution for Co did decrease the γ' fraction by around 10 %.

To first order, densities can be estimated from the average atomic mass of the alloy. For the base alloy, a density estimate of 9.36 g cm⁻³ was extrapolated from the Ni-base superalloy RR1000, whereas the experimentally obtained density was 9.18 g cm⁻³, $\sim 2\%$ lower than would be expected. The density for the alloy variants studied here can then be extrapolated from that for the Co-7Al-7W base alloy on the same basis. Since Mo is in the period above W, the substitution of Mo for W does have the benefit of reducing the density (7 at.% W corresponds to around 20 wt.%) albeit at the cost of lowering the γ' solvus temperature. The density reduction observed is very similar to that expected. However, additions of Ni for Co or Ta for W would not be expected to have a pronounced effect on density; in each case, the measured densities are around 1 % higher than would be expected from the average atomic mass of

the actual alloy compositions (*i.e.* after controlling for melting errors). Similarly, the 2Ti alloy would be expected to have a density slightly lower than the base alloy, at 9.03 g cm^{-3} , but actually has a density of 9.16 g cm^{-3} , 1.4% higher than expected and very similar to that of the base alloy. These effects cannot be attributed to experimental uncertainty, which is on the order of 0.1%.

These greater-than-expected densities are a reflection of the effect of these alloying elements on the lattice parameters of each phase, and the phase fractions (see Table 3).

Microstructures

A fine-grained hot rolled microstructure was observed using optical microscopy in all of the samples, shown in Figure 3a for the base alloy. The grains were very commonly found to be twinned, which is expected due to the low stacking fault energy of Al Co.

The microstructures obtained after subsolvus aging are shown in Figure 3. A conventional superalloy microstructure composed of cuboidal γ' in a γ matrix was observed in all the alloys, but with varying average γ' size. The base and 2Mo alloys possessed very small γ' , on the order of 20 nm in size. In contrast, the 2Ti and 20Ni alloys possessed much larger, 50–80 nm γ' . Coarsening was found to be more rapid in the 2Ta alloy, with only 100 h aging resulting in $\sim 200 \text{ nm}$ γ' precipitates. However, it should be noted that because the aging was performed at a fixed temperature relative to the solvus, this sequence mirrors the aging temperatures. The 20Ni alloy ($\sim 80 \text{ nm}$) coarsened more rapidly than the 2Ti alloy (50 nm), since these were aged at the same temperature. In general, the γ' could not be observed by SEM after furnace cooling from the solution temperature, or after aging for $< 50 \text{ h}$. The only exception was the 2Ta alloy, where aging at 900°C for 50 h resulted in 50 nm γ' .

TEM examination of all the alloys was complicated by the magnetic behaviour of Al Co, which made examination of a randomly oriented grain in an electropolished specimen, Figure 4a, rather complicated. Therefore, electron backscatter diffraction (EBSD) was used to identify a grain for FIB-milling to observe the $L1_2$ γ' in the $\langle 100 \rangle$ zone. This then permitted an estimate of (i) volume fraction to be obtained, (ii) confirmation of the space group and superlattice of the γ' precipitate, (iii) to observe the existence of an additional fine-scale population of cooling γ' in

Figure 3: Optical microstructure for the base alloy (top left); Microstructures obtained in the first batch of alloys after the aging heat treatment (etched, secondary electron imaging).

between the $\sim 40 \text{ nm}$ γ' coarsened by aging, (iv) and to measure the channel width.

From these results, coarsening in these alloys appears to be much slower than in conventional Ni-base superalloys. This presents an opportunity, in that smaller γ channel widths may be attainable in Co-base superalloys than Ni, even for service-scale lifetimes, as it is generally supposed that the γ channel width is the major source of dislocation curvature. Therefore, dislocation strength in the high temperature, low stress tertiary creep regime may be significant. Whether these slow coarsening kinetics are a result of (i) the low diffusivity of W, (ii) a low solubility for γ' formers in the matrix or (iii) a low driving force for coarsening, is still unknown.

Figure 4: Microstructures obtained in the 2Ti alloy (Batch 1) after aging heat treatment; (a) electropolished, BF TEM, (b) DF in the [001], FIB-milled.

However, this effect may not be industrially significant; since Ta additions have been shown to raise the solvus temperature and the temperature at which the strength drops off, it seems likely that any commercial alloys will contain Ta. As we show here, the Ta containing alloys coarsen more rapidly. The ability to coarsen the γ' without incurring substantial energy and equipment costs, as well as avoiding evolution of the material in the early stages of component life, may prove commercially attractive.

Diffraction measurements

The synchrotron X-ray spectra obtained from integration of the entire diffraction rings are shown in Figure 5. Here, the resolution of the diffractometer is not particularly high; the peak width is on the order of $\Delta d/d = 0.5\%$. For this particular sample, the γ' superlattice peaks are readily discernible and therefore a Rietveld refinement of the lattice parameters of the two phases can be obtained. However, the superlattice peaks were only visible for the 2Ta and 2Ti alloys using X-rays. With neutron diffraction, the isolated superlattice peaks were not fit-able above background for any of the alloys; in the 2Ta alloy they were barely visible at HRPD, but were not at all in any of the other alloys. This is partially due to the relatively high background and low flux of neutron diffractometers compared to synchrotrons. The main fundamental h,k,l all odd or all even (*fcc*) peaks were separable using these higher resolution diffractometers, Figure 5(b-c); HRPD's backscatter bank has a resolution of $\sim 0.05\%$ whilst Vulcan's 90° bank has a resolution of 0.25% . In the present case, the resolution obtained using HRPD was limited by the sample mosaic, resulting in a peak width on the order of 0.25% . At Vulcan, in contrast, the

peak width obtained was around 0.5% , as might be expected from summing the width contributions in quadrature. Consequently, at HRPD the lattice parameters of both phases in all of the samples could be satisfactorily estimated, whilst Vulcan could only examine high lattice misfit samples and I12 only samples with adequate superlattice peaks. Therefore, it appears that the correct choice of diffractometer will depend on the element partitioning, which are generally unknown in this alloy system.

The evolution of the lattice parameter for each phase and the lattice misfit $\delta = 2(a_{\gamma'} - a_{\gamma}) / (a_{\gamma} + a_{\gamma'})$ with temperature for the 2Ta alloy are shown in Figure 6, from the I12 measurements. Of course, these are constrained values and the difference between the isolated phases is expected to be greater. From this data, the constrained thermal expansion can be estimated, Table 3. The fitting uncertainties from the Rietveld analysis are also given.

For the I12 data in the 2Ta alloy, the thermal expansion coefficient of the γ is found to be $13.4(1) \times 10^{-6} \text{ K}^{-1}$, which compares favourably with that of pure Co, $13.0 \times 10^{-6} \text{ K}^{-1}$. In contrast, the L_{12} phase is found to have a thermal expansion coefficient of $16.0(1) \times 10^{-6} \text{ K}^{-1}$. This results in the lattice misfit increasing with temperature. Here the room temperature lattice misfit was found to be $0.52(1)\%$, and rose linearly to $0.58(1)\%$ at 700°C . However, between 700 and 750°C the increase in lattice misfit appears to cease, which is at the point where dissolution of the γ' begins.

The second batch of the 2Ta alloy was found to have a slightly higher lattice misfit, of $0.67 - 0.72\%$. The use of two techniques, examining samples from the same melt in different texture orientations, provides an indicator of the robustness of the uncertainties estimated. In the 2Ti alloy, the HRPD and Vulcan measurements give room temperature lattice misfit value that are different by 0.1% . Thus, this is probably a better measure of the actual robustness of the lattice misfit measured. More importantly, the melt-to-melt variability in lattice misfit appears to be around $0.1 - 0.2\%$, corresponding to a 10 K variation in solvus temperature and a $\sim 1 \text{ at.}\%$ variability in each of the alloying elements.

The lattice misfit values increased in the order $2\text{Ta} > 2\text{Ti} > 20\text{Ni}$, regardless of the diffraction technique or melt. Therefore, the greater lattice misfit may be part of the reason that the 2Ta alloy coarsens more rapidly. Unusually, the thermal expansion of the two phases are also found to be very similar for the 20Ni

a) I 12 synchrotron diffraction spectra

b) HRPD neutron diffraction spectra c) Vulcan neutron diffraction spectra

Figure 5: Diffraction spectra obtained for the 2Ta alloy at room temperature (a) by synchrotron diffraction using an area detector, (b) and (c) using the HRPD and Vulcan TOF neutron diffractometers respectively. Red and black position markers correspond to γ' and γ peaks respectively.

Figure 6: Evolution of (a) lattice parameter for both γ & γ' and (b) lattice misfit with temperature for the 2Ta alloy, from the I12 measurements. The uncertainties estimated from the Rietveld refinement are shown.

alloy.

Compared to Ni-base superalloys such as CMSX-4, which has a room temperature lattice misfit of $\sim -0.3\%$ [19] and near-zero at temperature, the lattice misfit values in the present Co-base alloys are both different in sign and much greater in magnitude. This may have the benefit of enhanced coherency strengthening, or the lattice misfit may be so large that defects are produced in the interface. The

possibility that positive lattice misfit places the matrix into tension and therefore is undesirable should also be considered.

Oxidation

Figure 7a shows the mass change data against time from the cyclic oxidation experiments in air at 800°C . On the hypothesis that for a stable oxide scale to form, mass change should evolve with t^2 , the

Table 3: Lattice parameters and lattice misfit values, δ , for each phase measured *in situ* using synchrotron X-ray and neutron diffraction, both at room temperature and elevated temperatures, T . The change in lattice misfit with temperature and (constrained) thermal expansion of each phase, α , are also calculated, with uncertainty estimators from the Rietveld refinements. The neutron measurements are from the second melt whilst the X-ray measurements are from the first.

	room temperature			T	at temperature			$\Delta\delta/\Delta T$	$\alpha_\gamma \times 10^{-6}$	$\alpha_{\gamma'} \times 10^{-6}$
	a_γ (Å)	$a_{\gamma'}$ (Å)	δ (%)	(°C)	a_γ (Å)	$a_{\gamma'}$ (Å)	δ (%)	(% / 10^3 K)	(K^{-1})	(K^{-1})
I12 – synchrotron X-rays										
2Ti	3.5826(2)	3.5946(9)	0.33(2)	750	3.6177(1)	3.6362(6)	0.51(1)	0.25	13.6 (1)	16.1 (1)
2Ta	3.5818(3)	3.6004(2)	0.52(1)	700	3.6152(2)	3.6364(2)	0.58(1)	0.09	13.4 (1)	16.0 (1)
HRPD – high resolution neutron diffraction										
2Ti	3.5686(2)	3.5898(3)	0.59(1)	700	3.6023(2)	3.6259(3)	0.65(1)	0.08	14.1 (1)	14.9 (1)
20Ni	3.5704(1)	3.5829(1)	0.35(0)	700	3.6046(1)	3.6167(1)	0.34(0)	-0.01	14.2 (2)	13.8 (2)
2Ta	3.5775(4)	3.6017(8)	0.67(0)	600	3.6058(1)	3.6314(2)	0.71(1)	0.07	13.9 (2)	14.4 (2)
Vulcan – medium resolution neutron diffraction										
2Ti	3.5691(4)	3.5941(6)	0.70(2)	500	3.5941(7)	3.6246(8)	0.84(3)	0.30	16.1 (2)	18.3(2)
20Ni	3.5685(6)	3.5885(6)	0.56(2)	150	3.5727(5)	3.5944(6)	0.61(2)	–	–	–
2Ta	3.5746(5)	3.6004(7)	0.72(2)	600	3.6126(7)	3.6382(6)	0.70(2)	-0.04	18.7 (3)	18.9 (2)

parabolic rate is also shown in Figure 7b. However, it should be noted that all of the samples examined appeared to suffer from spallation on cooling.

The mass gains recorded were on the order of $10\times$ larger than that of a commercial Ni-base superalloy that possesses a stable chromia or alumina scale. This is expected, as cobalt oxide is not protective. However, it is observed that Mo substitution for W results in significantly worse behaviour, whilst 2Ta substitution for W approximately halves the oxidation rate. Ti and Ni additions appear to have minimal effect on the oxidation behaviour.

The oxide scales were all similar in morphology and phases observed, so only the 2Ta alloy will be discussed, Figure 8. At the outer surface, the nominal stoichiometry of the oxide was approximately CoO. A series of voids were then observed at the interface to another oxide subscale containing approximately 50 at.% O content. It should be noted that both a CoO and a Co_3O_4 oxide can exist; the X-ray diffraction measurements or TEM examination to make a definitive determination have not been performed. At the interface to the metal, a further series of voids were observed; in both cases these are presumably due to the Kirkendall effect. In the outermost metal layers, Co_3W precipitates are observed with a characteristic high aspect ratio morphology; this region is also denuded of γ' .

The reason for this appears to be that the inner oxide layer has a high Al content. In contrast, the

Figure 7: (a) Mass change data for the alloys from the cyclic oxidation experiments. (b) Mass change data for Co-base alloys from oxidation experiments plotted as (mass change)² against time.

outermost oxide layer contains very little Al or W. Therefore, as with superalloys, the preferential removal of Al from the surface into the oxide results in the formation of undesired phases. As is well under-

Figure 8: Secondary electron image of the 2Ta alloy after 196 h exposure in air at 800 °C. An EDX map is also shown of the highlighted area.

stood, if the Al:W ratio decreases too far, then the familiar Co_3W precipitate is formed instead of γ' .

Discussion

The present work confirms the findings of other authors that stable $\text{Co} - \text{Co}_3(\text{Al},\text{W})$ microstructures can be produced. In addition, we have shown that a conventional ingot metallurgy route to produce fine grained hot deformed polycrystalline material may be feasible. As is well known, alloys based on pure Co possess poor oxidation resistance. Here, Ta additions have been found to be beneficial whilst Ni additions, of themselves, have only minimal effect on oxidation behaviour. However, Ni additions may allow higher Cr additions to be made without destabilising the γ - γ' microstructure. Here, we have verified that substantial Ni additions can be made whilst still producing a conventional phase assemblage; these also result in slightly higher solvus γ' temperatures.

The diffraction results indicate that the micromechanics of Co-base superalloys will be slightly different to those of Ni-base superalloys, because of the large and positive lattice misfit observed, albeit similar dislocations configurations have been found in the yielding regime by Suzuki *et al* [2]. It is also found that the thermal expansion of the γ' is greater than that of the γ , so the lattice misfit will only increase

away from zero with temperature; the consequences of this are unknown. However, it is suggested by our 20Ni alloy that the thermal expansion of the two phases can be matched, which may allow for tailoring of the lattice misfit at temperature to be performed both *via* the thermal expansion coefficient and the effect of alloying on the intrinsic lattice parameters.

Conclusions

Quaternary Mo, Ta, Ti and Ni substitutions in a Co-7Al-7W (at.%) alloy have been made and the resulting physical metallurgy examined. The following conclusions can be drawn.

- A polycrystalline ingot metallurgy process route appears to be feasible.
- The expected trends in γ' content, solvus temperature and density are reproduced; Mo lowers the density and solvus, Ti raises the solvus, Ni raises the solvus at a cost in precipitate fraction whilst Ta raises the solvus by over 150 °C. The 2Ta alloy also coarsened quite rapidly, and appeared to possess a further population of tertiary γ' .
- The CoO oxide scales formed are not protective and suffered from spallation on cooling during cyclic oxidation testing. Ta additions also appeared to improve the oxidation resistance.
- Positive lattice misfit between 0.3 and 0.7% were obtained, with the lattice misfit increasing with temperature. The thermal expansion coefficient of the γ' phase was found to be $14 - 18 \times 10^{-6} \text{ K}^{-1}$, depending on the alloy.

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