### OXIDATION AND HIGH TEMPERATURE CORROSION BEHAVIOUR

#### OF MODIFIED MCrAIY CAST MATERIALS

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# Summary

The influence of the composition of MCrAlY alloys and alloys doped with additional elements (Ta, Ti, Si, Zr, Mm) has been studied with respect to their cyclic oxidation and corrosion resistance behaviour, the object being to optimize these systems for application in heavy duty industrial gas turbines.

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#### Introduction

Coatings used at high temperatures in heavy duty industrial gas turbines have to satisfy a number of requirements which include oxidation and sulphidation resistance. The alloys used as coatings are chosen predominantly from the MCrAlY (M = Ni, NiCo, Co or Fe) group of materials.

The aim of the work described is to increase the corrosion and oxidation resistance of MCrAlY (M = Ni, NiCo,Co) systems using low levels of additional elements (Si, Ti, Ta, Zr, Mn, etc.). The MCrAlY systems comprise a matrix and an intermetallic phase (NiAl or CoAl). The mode of corrosion inhibition involves the dissolution of the intermetallic to supply the surface with aluminium for  $Al_2O_3$  formation (1). The amount of intermetallic in the system determines the ductility which is normally very low (2). Therefore, the improvements available will be based on (a) using the existing matrix and phase solubility ranges without generating additional phases (reported here) or (b) deliberately exceeding the solubility limits in order to obtain more corrosion and oxidation resistant phases (to be reported at a later date). Modifications to intermetallics have been made to improve the oxidation and sulphidation resistance of a high strength alloy (3) and a LPPS coating (4).

A further centre of interest is the incorporation of Ta-rich phases into a ductile nickel or cobalt matrix. The inclusion of Ta in NiCrSi systems has shown a vast increase in oxidation resistance due to the formation and corrosion resistance of TaSi rich phases (5,6). Historically, work on the stabilization of geometrically close-packed phases has been continued for some years at the Centre de Recherches Métallurgiques (CRM), Belgium and attempts have been made to produce a stable FCC  $\cdot$   $\alpha$ -Co $_3$ Ta phase. However, this phase is unstable and converts readily to HCP  $\cdot$   $\beta$ -Co $_3$ Ta. Cobalt alloys which include this phase can be stabilized using Ni additions (for example S57) and these alloys have been shown to be extremely corrosion resistant (7,8).

The range of alloying elements was extended to include Mn and Zr as thermodynamic calculations have previously shown (1) that both elements increase the activity of Al in the NiCrAl matrix i.e. the probability of  $Al_2O_3$  formation is increased.

#### Experimental Procedure

The experimental procedure adopted here consisted of performing differential thermal analysis (DTA) to determine the range of matrix solubility and cyclic oxidation studies on cast specimens to follow the formation and adherence of protective scales. The nominal compositions of the alloys studied are given in Table 1.

DTA experiments were carried out using a Netsch DTA Type STA 409 with 10g specimens under argon (0,4 1/hr) at heating and cooling rates of 10 K/min. All specimens were heated and cooled twice. The second cooling curve was used for evaluation. Cyclic oxidation samples of selected compositions were cast to begin with in alumina crucibles ( $\emptyset$  16 mm) under argon (99,99%) using a HF generator. Porosity problems with several alloys led to the modification of this equipment to allow drop casting in vacuum. The Si version of the NiCoCrAlY alloy could not be cast without cracking occurring although NiCoCrAlY variations have been discussed in the literature (4,9) in the low pressure sprayed form (i.e. coatings prepared using atomised powder). Cyclic oxidation testing was carried out in air using a dwell period of 1 hour at 1000°C and  $\Delta T \simeq 50$  K/min in the slow mode with cooling to

approximately 100°C and  $\Delta T \simeq 500$  K/min in the fast mode. Specimens were weighed at regular intervals to allow specific weight gain curves to be drawn in the linear and parabolic form. Computer analysis was performed in order to determine the parabolic rate constants. Alloys were exposed to  $SO_2/SO_3$  in a salt immersion test at  $850^{\circ}$ C for 1000 h in order to study the corrosion behaviour. The composition of the salt mixture and experimental details are given elsewhere (10). All samples were sectioned, nickel plated and examined using optical and SEM methods. Analysis was carried out where necessary using an electron microprobe analyser. Attention was paid to determining stability effects and most microprobe work on exposed material was concentrated on analysing directly below the scale and approximately 100  $\mu m$  from the specimen surface. Information obtained in this way is invaluable in indicating the scale regeneration properties of the alloy.

	Ni	Со	Cr	A1	Y	Та	Нf	Si	Ti	Mn	Zr
NiCrAlY	Bal	_	17	5	0,7	_	-	3-3,5	3,5-4,5	1,5	<1
11	11	-	21,80	10,55	0,85	-	-	< 2,5	∿ 6	3	
11	**	_	25	5	0,50	_	-	3-4	3	3	<1
NiCoCrAY	11	23,60	18,00	12,81	0,41	_	-	< 2,5	√ 5	3	<1
CoCrAlY	_	Bal	28,24	6,41	0,95	_		1-2	2,5	∿ 5	<1
11	-	**	22,82	13,05	0,73	-	-	2,5	∿ 5	3	<1
11	25	11	25	5	0,50	-	_	3	5	3	<1
11	-	н	25	5	0,50			3	2	3	
11	10	**	25	3	0,50	5	-	< 2,5	< 2,5	1,5-3	
CoCrAlHf	_	11	25	10	<del>-</del>		3	6			

Table 1: DTA limits of matrix solubility (wt.%) of Si, Ti, Mn and Zr.

# Results and Discussion

DTA. The limits of maximum matrix solubility are shown in Table 1. It appears that a relationship exists between Al content and Si addition (probably due to the limited solubility between the two) for Ni base alloys. Increasing the Al content from 5 to 10,5 or 12,8 % reduces the Si content from 3-3,5 to Si < 2,5%. The addition of Co or variation of Cr content does not appear to affect solubility. The opposite appears to be true for Ti. Increasing the Al content increases the Ti content up to levels of Ti > 5with 12,8 % A1. These effects seem to apply to Co base alloys as well with Si and Ti increasing with Al content. The presence of Ni and Ta lead to a limited solubility although the Al content is low (3%). As expected from the literature (11-13) the solubility of zirconium in NiCrAl systems was shown using microprobe analysis to be extremely low. The solubility of Mn in CoCrAl is much higher than that of Zr. In the majority of cases Mn could be added in amounts up to 3 wt.% and in one case up to 5%. The effect of Mn appears to be the extension of the matrix solubility range i.e. the amount of intermetallic which precipitates is reduced as more Al can remain in

solution in the matrix. Systems containing Zr and Ni base alloys containing Mn are not discussed further.

# Cyclic Oxidation

Slow cyclic mode. Linear and parabolic plots were produced for each alloy tested and the parabolic rate constants are given in Table 2. At the slow cooling rate level ( $\Delta T \simeq 50~\text{K/min}^{-1}$ ), low additions of Si, Ti, Ta and Mn were not found to alter the parabolic rate constant to any great extent. The cast alloys generally formed adherent Al<sub>2</sub>O<sub>3</sub> scales and little spalling was observed.

Base Alloy	Addition in Wt%	Parabolic Rate constant $mg^2$ cm <sup>-4</sup> h <sup>-1</sup> $(x10^{-4})$ $(\Delta T \sim 50 \text{K/min})$	Parabolic Rate constant mg <sup>2</sup> cm <sup>-4</sup> h <sup>-1</sup> (x10 <sup>-4</sup> ) (∆T≃500K/min)	Sulphur Penetration S <sub>max</sub> (µm)	
Ni-16Cr-6A1-0,7Y	0	_	NP after 960h	20-30	
Ni-22Cr-11A1				**************************************	
-0 <b>,</b> 85Y	0	20,8	NP after 400h	-	
	2 Ti	24,8	-	<del></del>	
	2,5 Si	57,8	<del>-</del>	-	
Ni-25Cr-5A1					
-O <b>,</b> 5Y	0	2,6	3,86	∿ 60	
	3 Si	6,4	3,5-4,1	∿ 50	
	2 Ti	9,49	-	-	
	2,5 Si, 1 Ta	2,54	2,05	-	
	2,5 Si, 2 Ta	_	1,5	>100	
	2,5 Si, 3 Ta	2,46	15,9	>100	
Ni-24Co-18Cr					
-13A1-0,41Y	0	26,4	NP after 900h	40-50	
	2,5 Ti	53,6	-	_	
Co-29Cr-6A1					
-0,95Y	0	5,37	3,46	∿ 55	
	1 Si	1,92	3,35	√ 40	
	2,5 Si	46,84	<b>-</b>		
	1 <b>,</b> 5 Ti	10,95	<del>-</del>	-	
	2,5 Ti	209,9	-	-	
	3 Mn	26,7	8,9	∿ 80	
	5 Mn	not parabolic	_		
Co-25Cr-10Ni					
-5Ta-3A1-0,5Y	0	11,4	_	_	
	1 Si	0,72	2,63-5,6	<b>∼ 70</b>	
	2 Si	18,15	-	_	
	2,5 Si	747	_	_	
	1 Ti	0,896	NP	80-100	
ATD-AT . D 1 **	2 Ti	NP after 400h	-	_	
NP=Not Parabolic	2,5 Ti	NP after 40h	_	-	

 $\frac{\text{Table 2}}{\text{at }1000^{\circ}\text{C}}$ : Parabolic Rate Constants of cyclic oxidised alloys at  $1000^{\circ}\text{C}$  and sulphur penetration depths at  $850^{\circ}\text{C}$ .

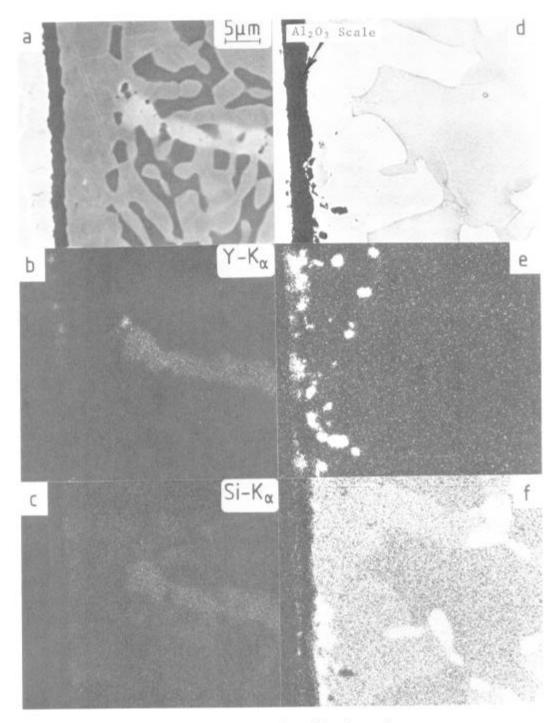


Fig. 1: Yttrium and silicon distributions in Co29Cr6Alo,95Y2,5Si (a,b,c) and Ni22Crl1Alo,7Y2,5Si (d,e,f) after cyclic oxidation (slow mode).

Microstructures of a Co and a Ni base system with their respective scales are shown in Fig.1. The exposed cast materials are characterised by a single phase field between the scale and the intermetallic compound. The scale thickness varied between 2-3  $\mu$  for Co systems and 5-7  $\mu$  for Ni systems. Pegging (14) and the presence of pegs could not be demonstrated although yttrium was associated with the Al<sub>2</sub>O<sub>3</sub> scale (15) in both systems. In the example shown in Fig. 1, the Si getters the yttrium in the Co base system producing a Si-Y phase. This is not the case with the Ni base system (Fig. 1) although reported in the literature (16).

The addition of Ti is beneficial at very low levels. An example of this is shown in Fig. 2 for CoCrNiTaAlY with 1,2 and 2,5% Ti. The sample with 2% Ti became unstable after 400 hours and the 2,5% Ti sample showed a weight loss after 40 hours of cyclic exposure. This effect is due to the presence of Ti disrupting  $Al_2O_3$  scale formation on both Ni and Co base materials. Furthermore the oxidation product is usually present in nodule form which is susceptible to spalling. Nodule formation is shown in Fig. 3 for Co25CrloNi3Al5Ta2Ti and Ni25Cr5AlO,5Y2Ti together with a typical  $Al_2O_3$  scale as found in this study.

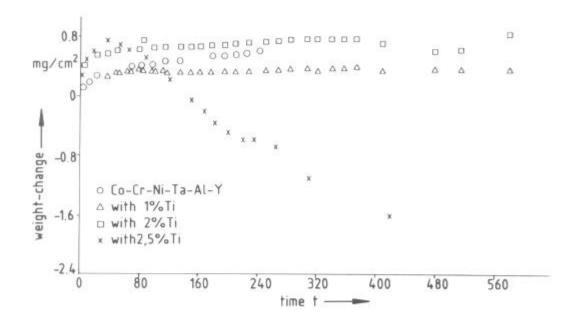


Fig. 2: Effect of Ti on the specific weight change of CoCrNiTaAly.

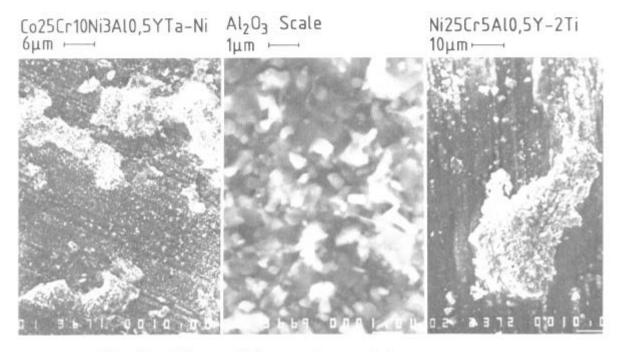


Fig. 3: Effect of Ti on scale morphology.

Fast Cyclic Mode. Raising the cooling rate from 50 to 500 K/min<sup>-1</sup> produces various changes with regard to the alloying addition and parabolic rate constant. Fig. 4 shows linear plots for four cast Ni base systems of different composition. The alloys with low Cr:Al ratios exhibit weight losses and surface spalling of Al<sub>2</sub>O<sub>3</sub> (Fig. 5). Only the Ni25Cr5AlO,5Y alloy exhibits an Al<sub>2</sub>O<sub>3</sub> scale (Fig. 5) without spalling. Under these conditions, the addition of Si does not vary the parabolic rate constant to any significant degree. Although little testing of Ti containing alloys was carried out at  $\Delta T = 500$  K/min<sup>-1</sup> due to the weight losses found with  $\Delta T = 50$  K/min<sup>-1</sup>, the addition of 1%Ti to CoCrAlNiTaY proved negative and led to an extremely high oxidation rate within a short period of time. The low parabolic rate constants found with Si-Ta containing alloys were also measured at  $\Delta T \sim 500$  K/min<sup>-1</sup> with a minimum being found in the system Ni25Cr5AlO,5Y containing 2,5%Si and 2%Ta (see Table 2).

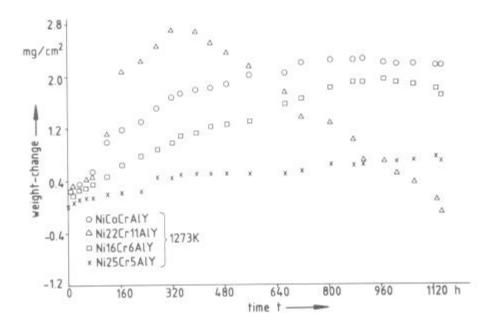


Fig. 4: Effect of rapid cooling on the cyclic oxidation behaviour of NiCrAlY(Co) alloys (Exact compositions, see Fig. 5).



Fig. 5 : Scales on NiCrAlY(Co) alloys after cyclic oxidation.

# Corrosion Resistance of Cast Alloys

As has been seen often in the past, the assessment of an alloy system can only be made after carrying out oxidation and corrosion tests. The corrosion test chosen here for screening purposes is a slag immersion test which produces the corrosion morphology found in large industrial gas turbines but within a reasonable period of time (1000-5000 hours). An example is shown in Fig. 6 for NiCoCrAly exposed at 850°C for 1000 hours. The S-Ka distribution shows a metal penetration between 40 and 50 µm. The penetration depths of the samples tested are given in Table 2. In general the effect of Si is to reduce the depth of sulphur penetration and the effect of Ta, Ti and Mn is to increase the depth of penetration. Fig. 7 shows the Si, S and Ta distributions of an Co25Cr10Ni3Al5TalSi0,5Y alloy following testing where sulphur is found in connection with the Ta, Si rich phases and Si dissolves out of the Ta rich phase and concentrates in the corrosion zone. Large depths of sulphur penetration are also found in Ni base alloys in connection with Ta additions.

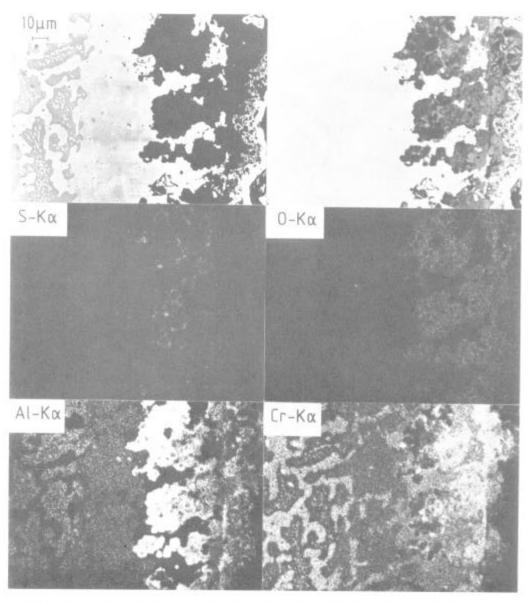


Fig. 6 : Scale formation and Sulphur penetration on NiCoCrAlY.

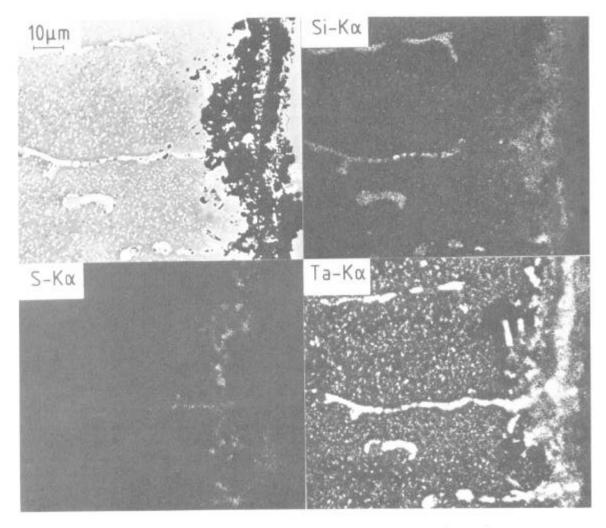


Fig. 7: Silicon, Sulphur and Tantalum distributions in Co25CrlONi3AlO,5Y5TalSi following corrosion testing at 850°C.

## Conclusions

The matrix and phase solubility ranges in existing systems can be modified without generating additional phases using low elemental additions and the following conclusions may be drawn:

- (1) Differential thermal analysis (DTA) can be used to determine the limits of matrix solubility of standard alloys for additions of Si, Ti, Mn, and Zr. The level of addition is altogether relatively low (3-5 %) and in the case of Zr < 1 % without causing additionally phase formation.
- (2) The addition of Si and Ta at low levels is shown to be beneficial regarding cyclic oxidation. The addition of Si to a yttrium bearing alloy causes a gettering of the yttrium and the formation of an oxidation resistant Si, Y phase. The presence of Ti disrupts the formation of the Al<sub>2</sub>O<sub>3</sub> scale and is susceptible to spalling.
- (3) Silicon is shown to be beneficial regarding resistance to sulphur penetration. Sulphide formation is enhanced by additions of Ti, Ta and Mn.