SEM and TEM Investigations on a Cr-Ni-Co Superalloy

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(Received May 10, 1999)

ABSTRACT

Chromium (Cr) – nickel (Ni) – cobalt (Co)-based superalloys are used in structural parts of steel annealing furnaces. This application requires the alloy to be modified by silicon (Si) to enhance the service life. This investigation firstly attempts to identify the microstructural changes that occur following silicon modification of the Cr-Ni-Co superalloy in as cast and heat treated conditions and then goes on to study the structure–high temperature properties correlations.

I. INTRODUCTION

Superalloys containing VIII-A group elements exhibit superior mechanical and corrosion properties at high temperatures. In service, superalloys are called upon to show high creep strength, thermal stability and corrosion resistance /1-4/. Microstructural changes occurring during casting and heat treatments impart such properties to these alloys. Microstructure in the as cast condition consists of FCC austenite and intermetallic phases which are mainly GCP (geometrically close-packed) γ' and γ'' phases and TCP (topologically close-packed) σ, μ and Laves phases. Besides these intermetallics, carbides, nitrides, borides and carbonitrides are also present; these may be stable or may transform from one to another /1,5,7/.

The Cr-Ni-Co based superalloy investigated in this work is mainly used in steel annealing furnaces as the support material on which steel bars roll. This alloy has a low thermal conductivity and a high wear resistance. In order to increase the high temperature service life of this alloy, silicon modification is essential.

The aim of this work was to identify the microstructural changes brought about by silicon modification in both cast and heat treated conditions and to study structure–high temperature properties correlations.

2. EXPERIMENTAL PROCEDURE

The alloy used in the present work was prepared by air melting in an induction furnace and casting in preheated cylindrical ceramic moulds. The chemical composition of the alloy is given in Table 1.

Silicon modification was accomplished by the addition of 0.48 and 4.20 wt% Si. Samples in the cast and heat treated conditions were examined by optical microscopy, scanning electron microscopy (JEOL 6400 (SEM) equipped with EDS and WDS) and transmission electron microscopy (JEOL 100C TEM). Phase determination was carried out by a Philips 1020 2FW X-ray diffractometer.

3. EXPERIMENTAL RESULTS

The typical microstructures of the Cr-Ni-Co superalloy containing 0.48 and 4.20 wt% Si respectively, in the as cast condition are shown in Figure 1. It is clear that increasing amounts of silicon resulted in an increase in the amounts of precipitate phases present the microstructure of the alloys. SEM micrographs (Figure 2) show that in both the silicon

Table 1
The chemical composition of the alloy used in the investigation

Element	C	Cr	Ni	Co	Mo	W	Fe	Mn
wt%	0.11	28.6	21.6	20.8	5.2	3.5	14.0	0.61

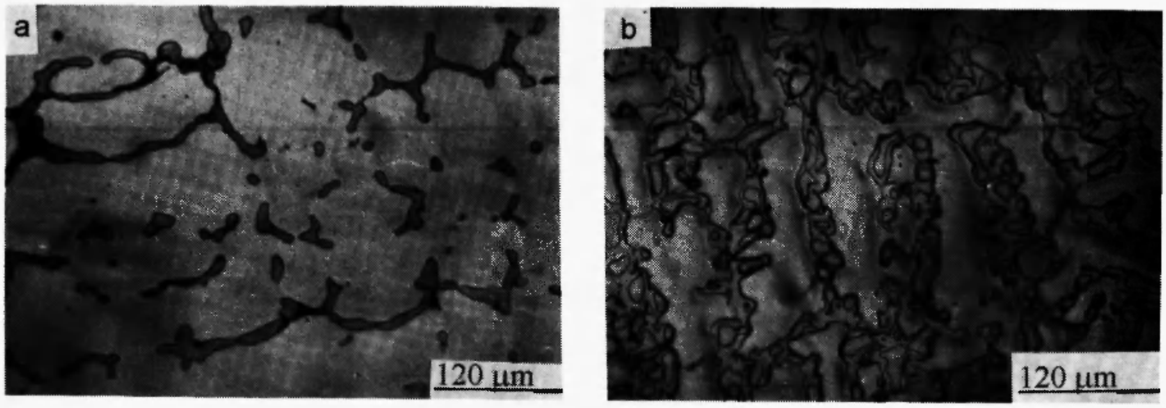

Fig.1: The microstructures of the Cr-Ni-Co superalloy (as cast). a) 0.48 wt% and b) 4.20 wt% silicon.

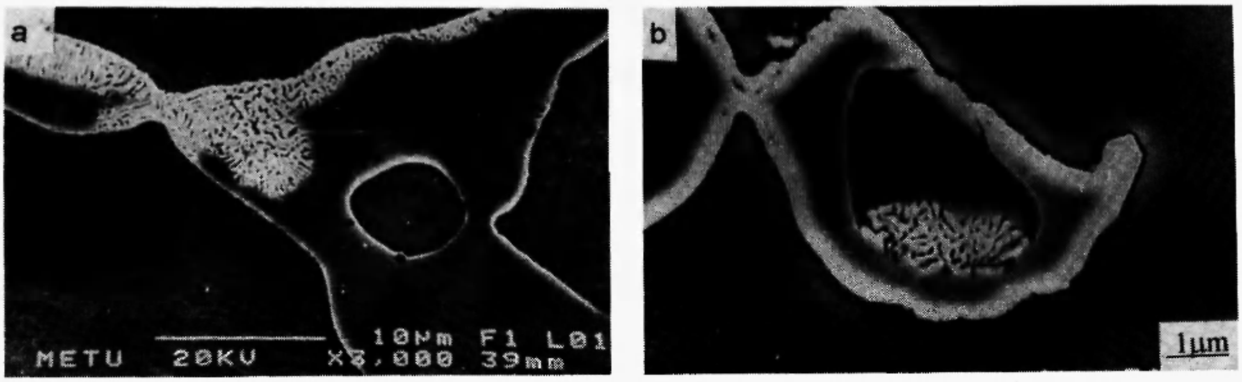

Fig.2 : SEM micrographs of the Cr-Ni-Co superalloy containing a)0.48% and b) 4.20 wt% silicon.

modified alloys the main precipitate phase present in the FCC austenite is the TCP tetragonal sigma phase. In addition, the BCC chi phase is formed within the TCP phase and cellular $Cr_{23}C_6$ carbide phase is present in the vicinity of the austenite-sigma interphase.

High silicon addition resulted in increased amounts of precipitate phases in the matrix and in the decomposition of the massive sigma phase which tended to increase the surface are of the chi phase formed in the sigma phase. Lower amounts of silicon caused lamellar type $Cr_{23}C_6$ carbide to precipitate at matrix-sigma interfaces. The size of the lamella was smaller than that alloy containing high silicon. Representative electron diffraction patterns obtained from these alloys are shown in Fig. 3. The typical microstructure of the heat treated silicon modified alloys is presented in Fig. 4 and Fig. 5. These alloys were heat treated for 30 minutes and 25 hours at 900°C.

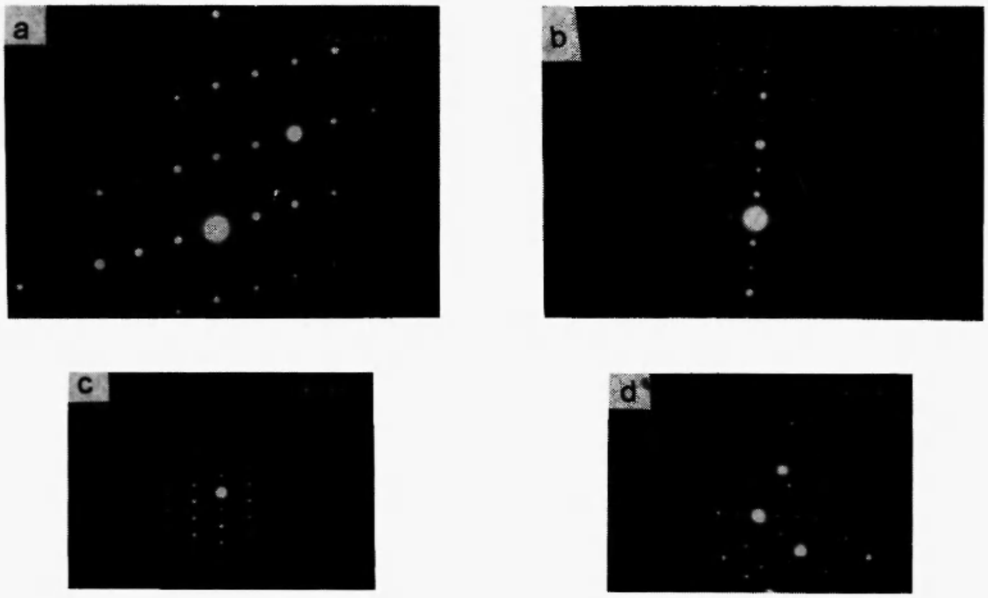

Fig.3 : Representative electron diffraction patterns from the Cr-Ni-Co superalloy (as cast), a) fcc austenite, zone axis $[\bar{1}13]$.b) Tetragonal sigma, zone axis $[00\bar{1}]$., c) bcc Chi, zone axis $[\bar{1}13]$., d) fcc $Cr_{23}C_6$ zone axis [013].

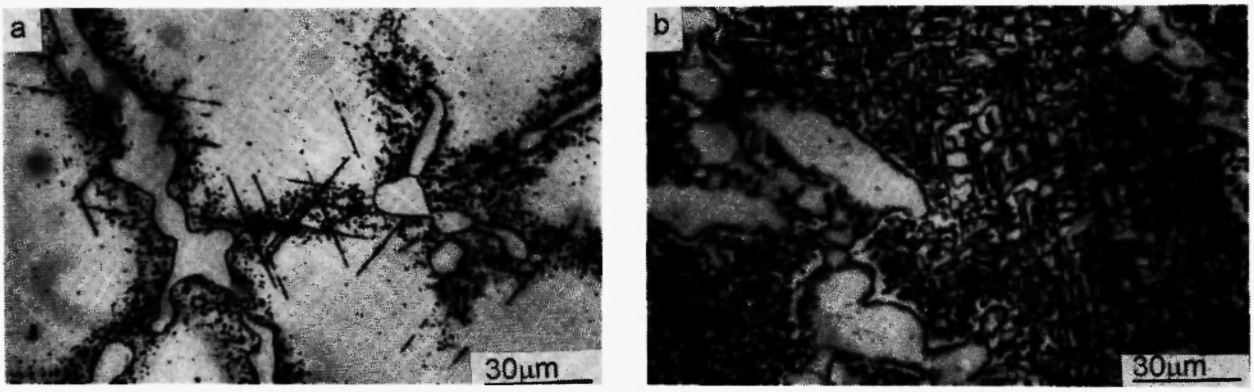

Fig.4 : Microstructure of heat treated alloys (for 30 mins at 900°C), a) 0.48 wt% and b) 4.20 wt% silicon.

The precipitation of fine particles around massive sigma phase regions is clearly visible in Fig. 4. From X-ray diffraction studies, these particles were identified as those of the tetragonal $Cr_{6.5}Ni_{2.5}Si$ phase (Table 2).

In higher holding times up to 25 hours, in alloy containing 0.48 wt% silicon precipitate phases were formed as long plates around fine spherical particles. These plates appeared to be smaller sized and covering the entire matrix in the alloy with higher silicon content (4.20 wt%), (Fig. 5).

Table 3 shows the various phases that occurred in the silicon lean alloy (0.48 w%) after heat treatment for 25 hours at 900°C. These phases were identified by x-ray diffraction as massive sigma, R, chi, $Cr_{6.5}Ni_{2.5}Si$ and Laves phases. The R phase formed by the transformation of sigma phase may be called an intermetallic phase and was not seen in the high silicon bearing alloy. The amount of precipitated phases increased with increase in silicon content (Figure 5).

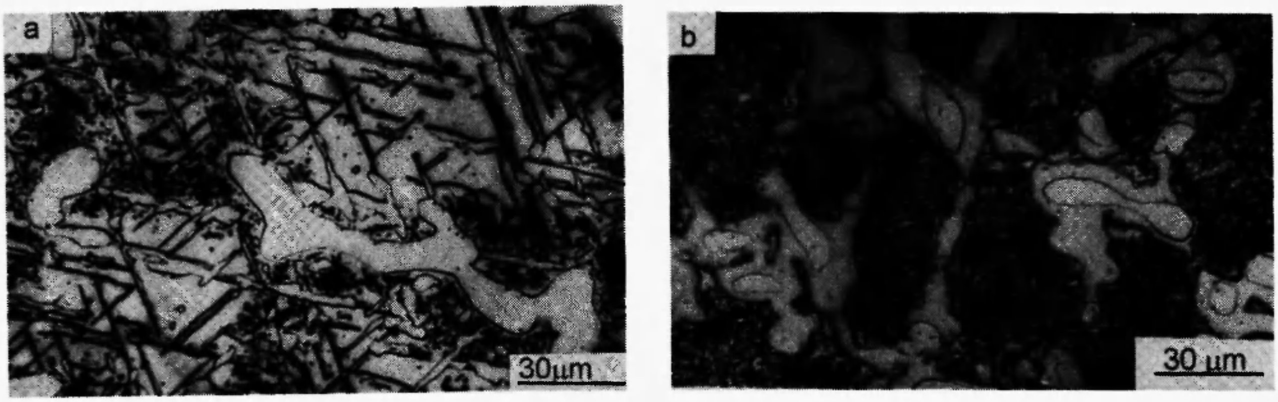

Fig. 5: Microstructure of alloys heat treated at 900°C for 25 hours, a) 0.48 wt% and b) 4.20 wt% silicon.

Table 2

X-ray diffraction data for 0.48 wt% si containing Cr-Ni-Co superalloy heat treated at 900°C for 30 mins (possible phases and planes)

d values (in this work)	Sigma Tetragonal /8/	$Cr_{6.5}$ $Ni_{2.5}$ Si Tetragonal (16-37)*	Chi, BCC (23-196)*	Austenite FCC (35-1489)*
3.129	3.11(220)			
2.837			2.83(310)	
2.794	2.783(310)			
2.396		2.382(311)		
2.279	2.273(002)			
2.139	2.135(410)	2.137(321, 112)		
2.078	2.074(330)	2.076(330)		2.08(111)
1.983		1.981(212, 420)		
1.943		1.935(411)		
1.901			1.90(332)	
1.886	1.883(222)	1.887(331)		
1.789	1		1.784(430)	1.80(200)
1.717	1.26(510)		1716(511)	
1.265		1.259(631, 532)	1.261(550)	1.26(220)
1.226			1.2258(641)	
1.211		1.208(701)	1.213(633)	
1.086			1.081(644)	
1.076				1.076(311)
1.054			1.051(822)	1.03(222)

*ASTM card number

Table 3
X-ray diffraction data for alloy containing 0.48 wt% si heat treated at 900°C for 25 hours (possible phases and planes)

d value (in this work)	Sigma, Tetragonal $Cr_{6.5}Ni_{2.5}Si$ (16-37)*	R, Hexagonal, CrCoMo (26-425)*	Chi, KYM $Co_{25}Cr_{25}W_8C_2$ (23-196)*	Sigma, Tetragonal Cr_3Ni_2 (26-430)*	Laves, Hexagonal (30-449)*
3.51					3.59(101)
2.79					2.79(102)
2.66		2.659			
2.60		2.599(131)			
2.39	2.38(311)		2.389(321)		
2.29	2.29(002)	2.299(134)		2.29(002)	
2.15		2.15(312,208)	2.16	2.15(410)	
2.07	2.07(330)				
1.98	(212, 420)			1.98(420)	
1.94			1.94(421)	1.94(411)	
1.89	1887(331)	1.89(1010, 235)	1.89(100)	1.89(331)	
1.79		1.79(02 10)			
1.54					1.54(210)
1.62	1.617(511)		1.62(521)		
1.33			1.329(542)		
1.32	1.32(621, 522)				
1.27		1.27(535)			1.28(106)
1.17	1.17 (641, 542)		1.17(730)	1.17(721)	
1.08			1.08(820)		
1.04			1.04(661)		
1.02			1.02(662)		1.02(400)
1.01			1.01(654)		1.01(401)
0.98					0.98(216)
0.89					0.89(217)
0.88					0.88(118)

*ASTM card number

4. CONCLUSION

The microstructure of the Cr-Ni-Co superalloy modified with Si, in the as cast condition, was found to consist of tetragonal sigma (σ) phase, BCC Chi (χ) phase which was located in the sigma regions and lamellar type $Cr_{23}C_6$ precipitates located near the sigma/matrix interfaces. Increasing silicon content tended to decrease the size of the sigma phase particles which caused an increase in the chi phase surface area; this resulted in the coverage of all matrix area. The formation of intermetallic phases in silicon modified alloys was interpreted to be directly related to the electronic properties of silicon. Since it is assumed that silicon electrons move up to the 3d level which is normally unoccupied, silicon behaved as a transition element. This was favourably for the formation of sigma and chi phases which are regarded as electronic compounds /9,10/.

In the Cr-Ni-Co superalloy heat treated for 30 minutes at 900°C the $Cr_{6.5}Ni_{2.5}Si$ phase precipitated and the amount of this phase rapidly increased with increasing amounts of silicon addition. Primary sigma phase tended to transform to R phase and a Laves phase showing a platelike structure was formed. In addition, the stability and formation of phases precipitated at high temperatures were found to be enhanced by silicon addition.

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