Effect of Microstructure on Hardness and Wear Resistance of a Silicon Modified Cr-Ni-Co Superalloy

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ABSTRACT

The secondary phases occurring in a Cr-Ni-Co superalloy, modified by silicon additions, have been identified. The microstructures of the alloy in the as cast and heat treated conditions have been examined and the effect of the silicon content on the resulting microstructure studied. The influence of the microstructure on the hardness and wear resistance of the alloy has also been investigated.

1. INTRODUCTION

The hardness and wear resistance of superalloys at elevated temperatures are considerably influenced by their microstructure. The changes in their properties are directly related to the amounts, distribution and morphology of the phases present in the microstructure. It is known that there are three different hardening mechanisms that are generally operative in superalloys and these are: (a) solid solution hardening contributed by the refractory metals (molybdenum, tungsten etc.), (b) carbide hardening due to the carbide forming elements present, and (c) precipitation hardening resulting from intermetallic phases like the γ' (gamma prime, A_3B) phase as a consequence of the addition of elements such as titanium and aluminium /1-5/.

Depending on chemical composition, intermetallic compounds which are detrimental to mechanical properties may also form during heat treatments or service. Intermetallics such as σ, μ and R, having topologic alloy close packed (TCP) structures, generally exhibit acicular or large faced morphology. These phases reduce high temperature fracture strength and weaken the γ matrix by depleting it in elements such as chromium. In order to control the formation of these phases, electron hole concentrations and probability of formation of these phases are determined /2,6-8/. The morphology and distribution of the phases present in the matrix remarkably affect the hardness and wear resistance of superalloys. TCP phase precipitates with acicular or blocky morphologies are particularly detrimental to tensile strength and ductility but they tend to improve high temperature fracture strength. This type of hard intermetallics are also known to affect the wear resistance properties and hardness of superalloys in a deleterious manner. Silence *et. al.* /9/ have shown that intermetallics directly influence the distribution of phases rather than the hardness. Focke *et al.* /10/ have contended that carbide morphology has important effects on wear resistance properties.

The influence of silicon on the formation of intermetallic phases has been studied by Boesch /11/. It has been shown that the addition of silicon increases the chemical stability gap where TCP type of sigma phase is stabilized. The stability of phases such as the G, μ, R and Laves phases have also been reported to be increased by silicon additions /12,13/.

Table 1

The chemical composition of the alloy used in the investigation

Element	C	Cr	Ni	Co	Mo	W	Fe	Mn	Si
Wt %	0.11	28.6	21.6	20.8	5.2	3.5	14.0	0.61	0.48

2. EXPERIMENTAL PROCEDURE

The chemical composition of the alloy used in the present investigation is shown in Table 1. This alloy will henceforth be referred to as a chromium-nickel-cobalt (Cr-Ni-Co) superalloy.

Alloys with the base composition without silicon were first melted in an air induction furnace and were then modified with silicon in the molten state; these were cast from 1580-1600°C in ceramic moulds preheated at 950-1000°C. Specimens obtained from the cast alloy were subjected to heat treatments for 30 minutes and 200 hours at 900°C and 1100°C.

The heat treated samples were etched electrolytically using an aqueous solution containing 10 wt% CrO_3 and then examined under a Zeiss Axiotech Vario optical microscope. A Jeol scanning electron microscope (Model 6400) was used for surface topography examination. For TEM studies, thin foils were prepared using a solution containing 20% sulphuric acid + 80% methanol in a twin / jet polishing equipment. Thin foils were then examined by a Jeol 100C TEM. X-ray diffraction studies were carried out using a Philips 1050 2FW-X diffractometer. Hardness tests were conducted in a Carl Frank universal hardness tester with a load of 100 kg. Wear resistance properties were measured with a CSM tribometer equipment (ball-on disc mode) at 200 rpm with a load of 10N, 2mm-wear diameter using WC-Co balls.

3. RESULTS AND DISCUSSION

3.1 Microstructure

The typical as cast microstructures of alloys containing 0.48 wt% Si and 4.20 wt% Si are shown in Fig. 1. The secondary phases present could be identified as sigma, chi and $M_{23}C_6$ carbide. $M_{23}C_6$ had formed at the matrix/sigma interface in a cellular morphology as a result of a eutectoid reaction. As seen in Fig.1, the amount of these phases increased with increasing amounts of Si addition.

The micrographs in Figure 2 show the representative microstructures of alloys containing 0.48 wt% and 4.20 wt% Si after heat treatment at 900°C and 1100°C for 30 mins. It is clearly seen that fine precipitates were formed around sigma phase regions after heating for 30 minutes at 900°C. A lenticular product comprising intersecting plates appeared after longer heating periods (up to 200 hours). The rate of precipitation was higher in the first 30 minutes of heating in the alloy containing

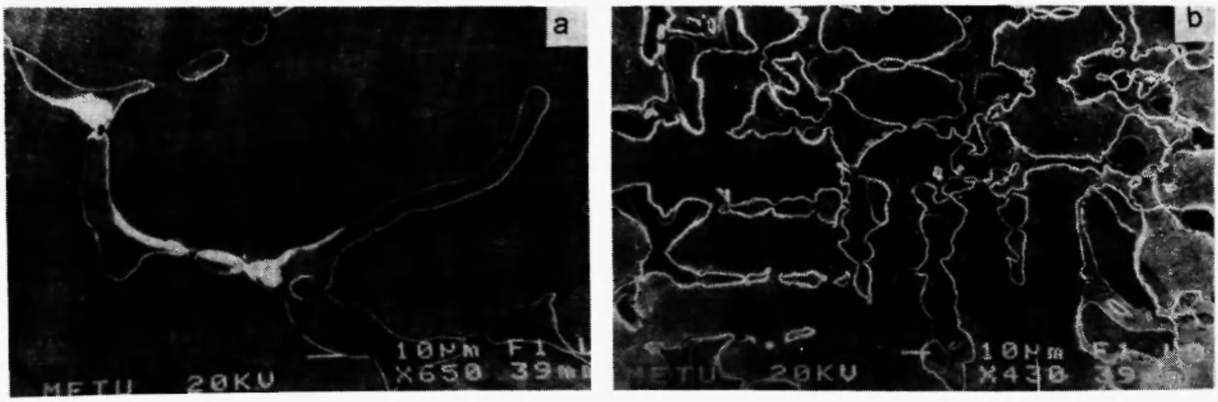

Fig. 1: SEM micrographs of alloys (as cast) (a) 0.48 wt% Si; (b) 4.20 wt% Si.

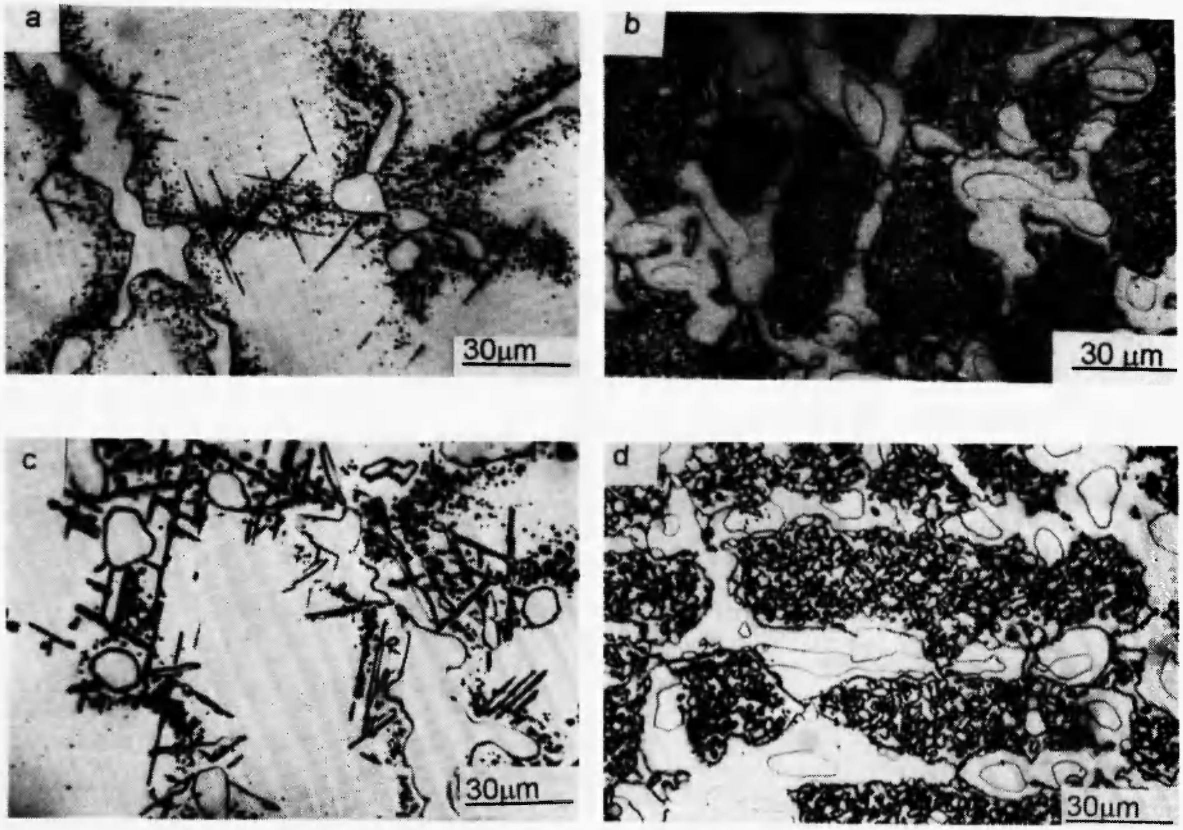

Fig.2: Microstructure of heat treated Cr-Ni-Co superalloys. a) 0.48 wt% Si, 900°C, 30 minutes; b) 4.20 wt% Si, 900°C, 30 minutes; c) 0.48 wt% Si, 1100°C, 30 minutes; d) 4.20 wt% Si, 1100°C, 30 minutes.

4.20 wt% Si. Some coarsening of the precipitated phases took place on heating for 200 hours. The microstructure of the low Si alloy, heat treated for 30 minutes at 1100°C, contained phases exhibiting a platelike morphology which formed in the early stages of heat treatment. This type of phases did not appear in this alloy with low Si content when heated for 30 minute at 900°C. In the high Si alloy the matrix was almost completely covered with precipitating phases after heat treatment. For the treatment at 1100°C, the precipitated phases showing an equiaxed morphology were coarser than those formed at 900°C. Fine particles occurring around the sigma phase regions tended to transform to another phase with increasing Si content.

The precipitated phase around the sigma phase regions was identified by electron diffraction to be the $Cr_{0.5}Ni_{2.5}Si$ phase. The lenticular phase formed after heating for 200 hours was identified as the $W_{13}Fe_{6.5}Si$ phase. Typical diffraction patterns corresponding to these two phases are shown in Fig.3.

3.2 : Mechanical properties

Hardness

The microstructural changes resulting from different Si contents markedly influenced the hardness of the alloys. The hardness of the Cr-Ni-Co superalloys in the as cast condition was sought to determined in terms of the macrohardness of the alloys (general hardness) and the microhardness of the microstructural constituents (various way phases present in the matrix).

It was not possible to define specifically the hardness of the sigma and chi phases from microhardness measurements. The hardness values determined are shown in Table 2. It was seen that increasing amounts of Si resulted in an increase in the general

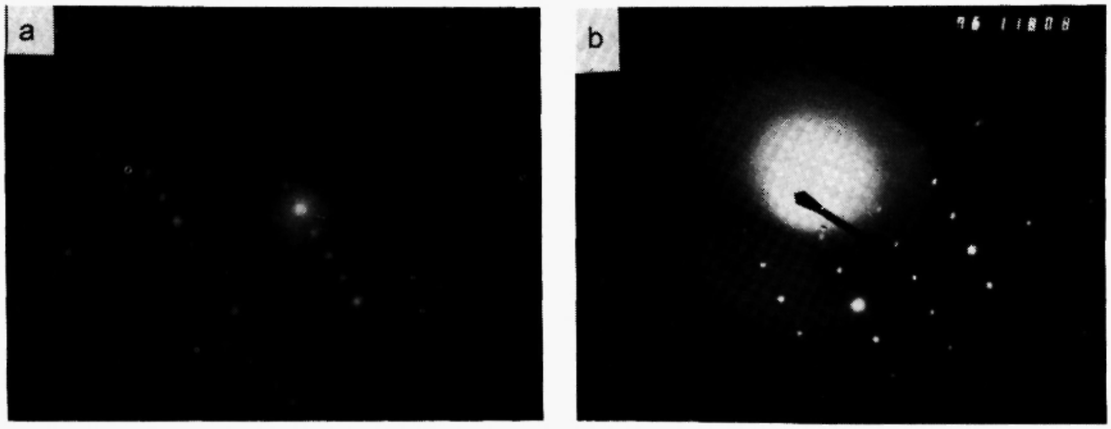

Fig.3: Electron diffraction patterns corresponding to the phases a) $Cr_{0.5}Ni_{2.5}Si$; b) $W_{13}Fe_{6.5}Si$.

Table 2
Effect of Si content on the hardness of cast Cr-Ni-Co superalloy

Wt% Si	General Hardness (HV) (kg/mm^2)	Matrix (HV)100 (kg/mm^2)	Phases* (HV) (kg/mm^2)
0.48	260	185	371.8
4.20	450	217.3	784.2

Table 3
Effect of Si content on the hardness of heat treated Cr-Ni-Co superalloy

	900°C		1100°C	
Wt% Si	30 mins	200 hrs	30 mins	200 hrs
0.48	258	339	283	276
4.20	628	615	533	491

hardness of the alloys. This increment in hardness was directly related to the amount of secondary phases promoted by the higher silicon content. Hardness values corresponding to the secondary phases varied form 370 HV (kg/mm^2) to 785 HV (kg/mm^2) with silicon content varying from 0.48% to 4.20%.

The observed variation in hardness values as a function of time after heat treatment at 900°C and 1100°C is shown in Table 3. The maximum hardness value of 784.2 HV was obtained in the as cast alloy containing 4.20 w% Si. Although hardness decreased with increasing heat treatment temperature, for identical treatment the hardness of the high Si alloy was greater.

It is generally assumed that hardness losses at high temperatures is partly due to the coarsening of secondary phases precipitated in the matrix and also to the partial decomposition of primary phases.

From Table 3 it is seen that hardness in heat-treated conditions depend significantly on Si addition. Higher Si content increases hardness as a result of more extensive precipitation of secondary phases.

Wear

Wear resistance is one of the most important properties of Cr-Ni-Co superalloys, since it characterizes the performance of the material under the prevailing service condition. Wear life at high temperatures is strongly influenced by microstructural stability. In the present work the effect of Si modification on the wear properties was examined and the results are presented in Fig. 4 and Table 4. The figure shows a typical wear curve obtained by using the ball on disc method from the alloy containing 4.20% wt% Si. Table 4 shows experimental results corresponding to the alloys containing 0.48 and 4.20 wt% Si.

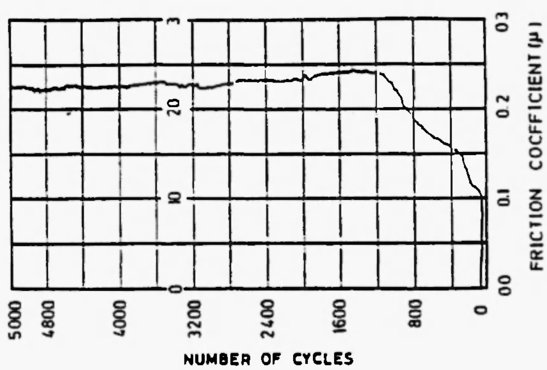

Fig. 4: Typical wear curve for alloy containing 4.20% Si.

accelerate the precipitation of intermetallic phases having large surface areas at the expense of the soft matrix. Since a large fraction of the matrix surface is covered by hard and brittle secondary phases, improvement in wear properties is expected to occur with higher silicon contents.

The type of Cr-Ni-Co superalloy selected for this work is generally subjected to service conditions conducive for wear to occur. These alloys are used in steel annealing furnaces as support materials on which steel bars roll. However, they maintain their mechanical stability at 900-1200°C for about 6 months.

The alloy containing 4.20 wt% silicon, heat treated at 1100°C (Table 5), showed the minimum wear rate. The microstructure of this alloy comprised second phase particles with large surface areas. The matrix was almost completely covered with these hard and brittle phases.

That the size, distribution and morphology of secondary phases have a major effect on wear properties is also reported elsewhere (10). Wear experiments carried out on cast samples at room temperature clearly

Table 4
Wear properties of Cr-Ni-Co superalloy (as cast condition)

Wt% Si	Wear rate (10^{-4} mm^3/m)	Wear volume (mm^3)	Wear depth (mm)
0.48	19,80	0.1247	0.0266
4.20	1,02	0.0064	0.00419

Table 5
Wear properties of heat treated Cr-Ni-Co superalloys

Wear rate $10^{-4}m^3/m$				
Wt% Si	900°C		1100°C	
	30 mins	200 hrs	30 mins	200 hrs
0.48	0.21	0.6434	0.5867	0.5617
4.20	0.4656	0.302	0.2283	0.0602

A significant reduction in the wear rate with increasing Si content could be clearly seen. Wear properties such as wear depth and wear volume also showed a similar dependence on the Si content as the wear rate. Increasing amounts of silicon probably showed the relationship between the morphologies of phases and the wear properties.

The wear behaviour is directly controlled by the morphology of second phase precipitates. The occurrence of the minimum wear rate in the alloy containing 4.20 wt% Si, heat treated at 1100°C, was due to the coverage of the matrix by primary phase and secondary phase precipitate particles (Table 5). This sort of microstructure inhibits contact with the soft matrix during service and reduces the wear rate of the alloy considerably.

The minimum wear rate and wear volume were obtained in the alloy containing 4.20% Si after heat treatment for 200 hours at 1100°C. The wear properties and the hardness of the alloy exhibited similar trends with regard to the influence of the Si content.

The improvement in wear resistance resulting from higher Si content could be ascribed to the fact that hard and brittle intermetallic phases effectively covered the softer matrix. Higher wear rates are observed after longer heating periods due to the coarsening of the precipitates of this phases.

4. CONCLUSIONS

In the case of silicon modification, the amount of silicon necessary for deoxidation is increased and the microstructure of Cr-Ni-Co superalloys changes. Silicon promotes the formation of intermetallic phases (sigma and chi).

Silicon plays an important role in the improvement of the wear properties of Cr-Ni-Co superalloys. Wear rates at room temperature decrease with increasing amounts of silicon. This is related to the morphology, size and distribution of the precipitates of intermetallic phases. An increase in the amount of phases showing large surface area and hard and brittle behaviour results in lower wear rates.

The precipitation of secondary phases occurs in Cr-Ni-Co superalloys on heat treatment at 900°C and 1100°C. Heating for 30 minutes at 900°C and 1100°C causes the formation of second phase particles. These are of the sigma phase and of the $Cr_{6.5}Ni_{2.5}Si$ phase, equiaxed precipitates of which form around the sigma phase regions. Lenticular precipitates of Laves phases tend to precipitate with longer heating times. The amount of the various intermetallic phases in the same heat-treated condition increases with increasing amounts of silicon.

Silicon promotes the formation of second phases in the matrix at high temperatures during casting. During the heat treatments carried out at 900°C and 1100°C, lamellar $M_{23}C_6$ precipitates (formed at the matrix/sigma and sigma/chi interfaces) tend to dissolve.

The size and distribution of second phase particles strongly influence the mechanical properties of Cr-Ni-Co superalloys. The wear rate is reduced with higher silicon contents. The minimum wear rate is obtained in the alloy containing 4.20 wt% silicon after a heat treatment for 200 hrs at 1100°C. The lower rate is due to the formation of equiaxed second phase precipitates showing large surface area.

Hardness tends to increase with higher silicon contents in all experiments carried out at 900°C and 1100°C. However, as expected, an increase in the heat treatment temperature lowers the hardness values. Higher hardness resulting from higher silicon contents is related to the enhanced precipitation rates of second phases and also to the size and distribution of the precipitates.

REFERENCES

1. C.T. Sims, N.S. Stoloff and W.C. Hagel, *Basic Alloy Systems, Superalloys II*, Wiley, New York, 1987; pp. 59-214.
2. L.R. Woodyatt, C.T. Sims and H.J. Beatti, Prediction of Sigma-Type Phase Occurrence from Composition in Austenitic Superalloys, *Transactions of The Metallurgical Society of AIME*, **235**, 519-527 (1966).
3. E. Hornbogen, Die Ursachen der hohen Warmfestigkeit von Superlegierungen, *Metall*, **36**. (5), 531-535 (1982).
4. T. Sims, The Role of Refractory Metals in Austenitic Superalloys, *6. Plansee Seminar,* 514-537 (1968)
5. W. Peter, H. Muller and E Kohlhaas, Einfluss von Kohlenstoff and Silizium auf die Eigenschaften der Kobaltbasis-Legierung X40CoCrNi4520, *Arschive fur das Eisenhuttenwesen*, 44 (1), 29-36 (1970)
6. J.R. Mihalisin, C.G. Bieber and R.T. Grant, Sigma-Its Occurrence, Effect and control on Nickel-Base Superalloys, *Transactions of The Metallurgical Society of AIME*, **42**, 2399-2414

(1968).

7. W.I. Mitchell, Uber das Aushartungsverhalten einer Nickelbasis, *Z. Metallkunde*, **55** (10), 613-616 (1964).
8. V. Biss, G.N. Kirby and D.C. Sponseller, The Relative Effects of Chromium, Molybdenum, Tungsten and Tantalum on The Occurrence of σ Phase in cast Ni-Co-Cr Alloys, *Metallurgical Transactions A*, 7**A**, 1251-1261 (1976).
9. W.C. Silence, Effect of Structure on Wear Resistance of Co-,Fe- and Ni-, Base, The International Conference on Wear of Materials, *The American Society of Mechanical Engineers,* New York, 77-85(1977).
10. A.E. Focke, F.E. Westermann, J. Kemphaus, W.T. Shih and M. Hoch, Wear of Superhard Materials when Cutting Superalloys, *The International Conference on Wear of Materials, The American Society of Mechanical Engineers*, New York, 228-237 (1977).
11. W. Boesch, Introduction – Superalloys; *Superalloys, Supercomposites and Superceramics,* Academic Press. Inc., New York, 1989; pp. 1-6.
12. D.I. Bardos, P.A. Beck, Electron Phases in Certain Ternary Alloys of Transition Metals with Silicon, *Transactions of The Metallurgical Society of AIME*, **236**, 64-69 (1966).
13. K.P. Gupta, N.S. Rajan, P.A. Beck, Effect of Si and Al on the Stability of Certain Sigma Phases, *Transactions of the Metallurgical Society of AIME*, **218**, 617-624 (1960).