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Development of an ultra-high-strength low-alloy NiSiCrCoMo steel

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Abstract. An ultra-high-strength low-alloy NiSiCrCoMo steel has been developed. The development work is part of a major programme at the Defence Metallurgical Research Laboratory in the field of ultra-high-strength, high-fracture-toughness steels. In this context we undertook investigations to understand the effect of solute additions on the fracture behaviour of Armco iron and Fe–C alloys. We investigated Fe–Ni, Fe–Co, Fe–Si, Fe–Mo, Fe–C–Ni and Fe–C–Co alloys for mechanical behaviour. The report by Garrison (1986) on a Fe–C–Ni–Si–Cr alloy was an important pointer to a low-alloy, ultra-high-strength steel with high fracture toughness. The material we have now arrived at is a Fe–C–Ni–Si–Cr–Co–Mo steel with tensile, impact and fracture toughness properties matching those of maraging steel 250 grade in tonnage scale melts.

Keywords. Ultra-high-strength steels; fracture toughness; maraging steel; tempered martensite embrittlement; segregation.

1. Introduction

More is known about steels, and more varieties of steels are in the marketplace, than any other class of materials. Even so, fresh understanding and development of new steels is a continuing endeavour because of the increased demand for structural integrity and reliability. Steels in several high-technology applications, such as aerospace, need to possess ultra-high-strength with high fracture toughness in order to meet the requirements of minimum weight and high reliability. It is well known that increase in strength is generally accompanied by a decrease in toughness. The existing ultra-high-strength low-alloy steels like AISI 4340, 300 M and D6ac (Metals Handbook 1992) can be used at yield strength levels > 1400 MPa. However, their use has been limited because of their lower fracture toughness compared to the other types of highly alloyed ultra-high-strength steels, like maraging steels and HP 9-4-30 (Metals Handbook 1992). We embarked upon a research programme with the aim of understanding the behaviour of fracture toughness of the base metal iron and its alloys and to develop ultra-high-strength fracture-resistant low-alloy steels. These results (Srinivas *et al* 1988, 1993; Srinivas 1991) have been utilized in combination with the work of Garrison (1986) on a Ni–Si–Cr steel to arrive at an Fe–C–Ni–Si–Cr–Co–Mo alloy. This paper describes briefly the development of this special steel, whose mechanical properties have been presented in comparison with the widely employed AISI 4340 and maraging steels.

2. Experimental

Thirty-kg melts of base steel (Garrison 1986) having composition 0·34 C, 3 Ni, 2 Si, 1 Cr in wt% and the same base steel with Co and/or Mo as alloying additions to the extent of less than 1 wt%, were vacuum induction-melted and processed to the required dimensions.

Tensile tests were carried out employing round specimens of 25 mm gauge length and 6·25 mm gauge diameter on a computer-controlled Instron 8500 servohydraulic test system at a nominal strain rate of $10^{-3}\,s^{-1}$. Standard charpy V-notch specimens were employed to measure impact toughness. Plane strain fracture toughness K_{IC} was measured employing 19·7 mm thick (3/4TCT) compact tension specimens in accordance with ASTM standard E399.

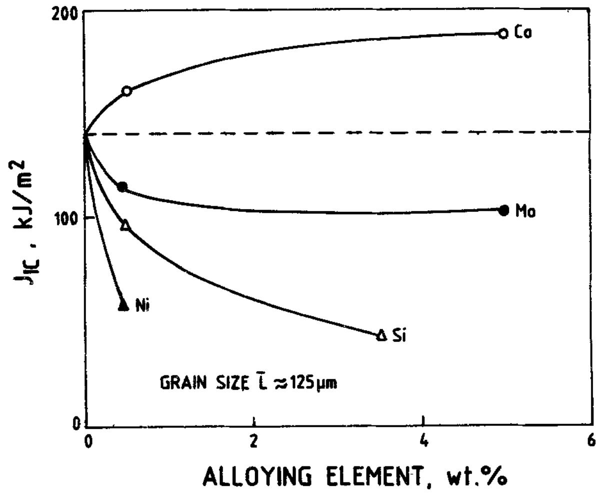

Figure 1. Influence of solute additions on fracture toughness of Armco iron at a constant grain size of ~ 125 μm.

Table 1. Mechanical properties of iron-based solid solutions and Fe–C–X alloys considered in the basic studies.

Material	YS (MPa)	UTS (MPa)	n	J_{IC} (kJ/m^2)
Armco iron	180	296	0·28	140
Fe–0·5Co	110	290	0·30	162
Fe–5·0Co	130	293	0·35	187
Fe–0·5Si	225	385	0·21	97
Fe–3·5Si	423	541	0·15	42
Fe–0·5Mo	187	359	0·27	112
Fe–5·0Mo	212	385	0·22	102
Fe–0·5Ni	195	335	0·25	59
Fe–0·2C	244	370	0·24	130
Fe–0·2C–5Co	242	409	0·25	232
Fe–0·2C–5Ni	297	467	0·19	153

3. Results and discussion

3.1 *Basic studies*

Basic studies (Srinivas 1991; Srinivas *et al* 1988, 1993) on the toughening behaviour of Armco iron as influenced by the alloying additions have revealed that, among the four alloying elements studied, namely cobalt, nickel, molybdenum and silicon, cobalt imparts significant improvement to fracture toughness (figure 1 and table 1). On the other hand, molybdenum, silicon and nickel are found to have a deleterious effect on fracture toughness J_{IC} of Armco iron (figure 1), with the least effect being noticed in the case of molybdenum. The increase in J_{IC} with cobalt addition can be understood in terms of the enhanced strain hardening exponent, n (table 1) and to the scavenging of carbon from grain interior to the grain boundary (figure 2; Srinivas *et al* 1993). The beneficial effect of cobalt with regard to J_{IC} observed with Armco iron was seen

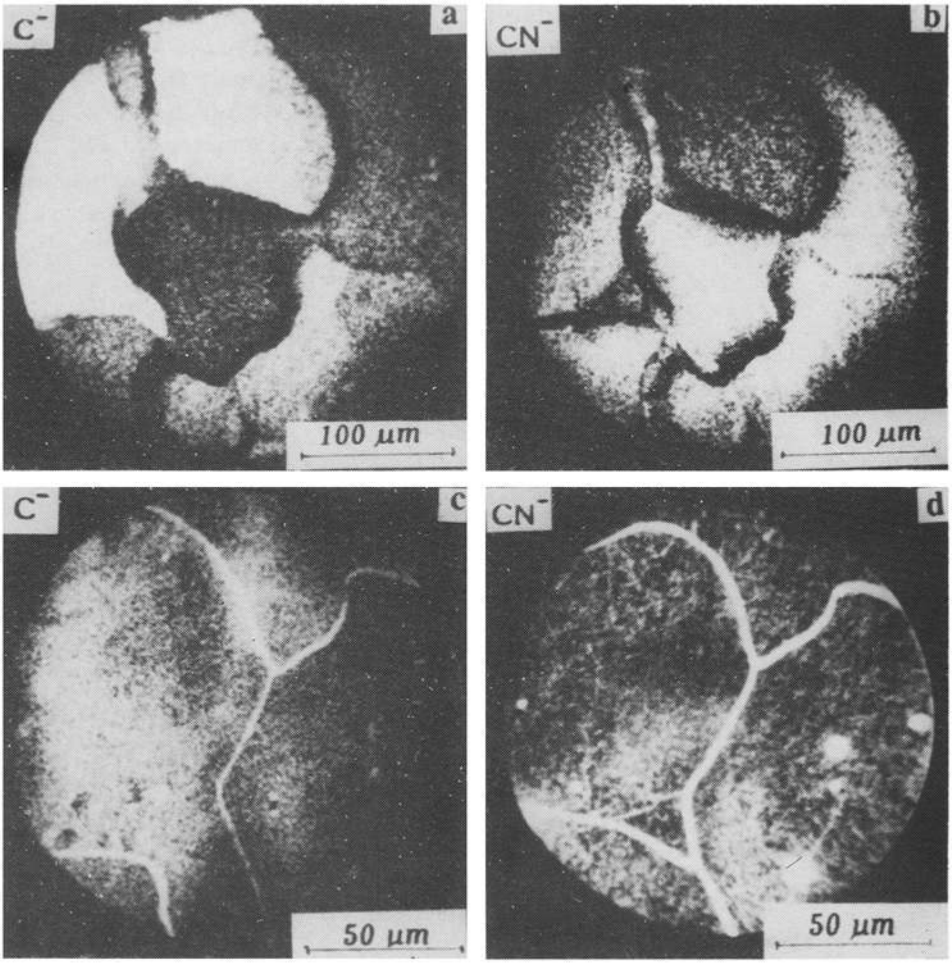

Figure 2. SIMS ion images showing (**a, b**) uniform distribution of interstitials in Armco iron, and (**c, d**) scavenging of interstitials to grain boundaries in Fe–5Co alloy.

to be even more pronounced in the presence of carbon (Srinivas *et al* 1991). With a 5 wt% cobalt addition the J_{IC} of Fe–0·2C alloy is enhanced nearly by 80% while maintaining the same level of strength (table 1). Nickel, generally considered to be a beneficial element in the presence of carbon, is seen to influence J_{IC} only marginally (table 1).

3.2 *Development of NiSiCrCoMo steel*

The tempering behaviour of the base Garrison steel was established and is shown in figures 3 and 4. The variation of strength with tempering temperature given in figure 3 shows that the steel retains high strength up to 300°C. Beyond about 350°C, there occurs a steep decrease in strength, which is also accompanied by a loss in ductility. A trough in ductility variation with tempering temperature occurs in the temperature range 400 to 600°C. The impact energy at room temperature increases with tempering temperature up to around 300°C, beyond which a steep fall occurs, with a minimum at 500°C (figure 4). A similar behaviour has been observed when impact tests were conducted at −40°C (figure 4). The data presented in figures 3 and 4 suggest that the steel develops an optimum combination of strength and impact toughness in the 250°C-tempered condition. Accordingly fracture toughness and ductile-to-brittle transition temperature (DBTT) were evaluated for the steel tempered at 250°C. A value of 103 MPa$\sqrt{\text{m}}$ for fracture toughness was obtained in valid fracture toughness tests conducted according to ASTM standard E399. The impact toughness in the

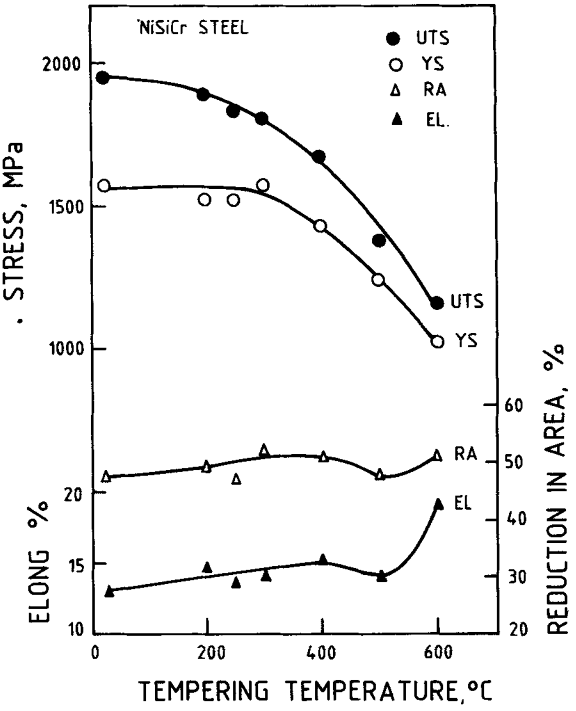

Figure 3. Tensile properties of NiSiCr steel as a function of tempering temperature.

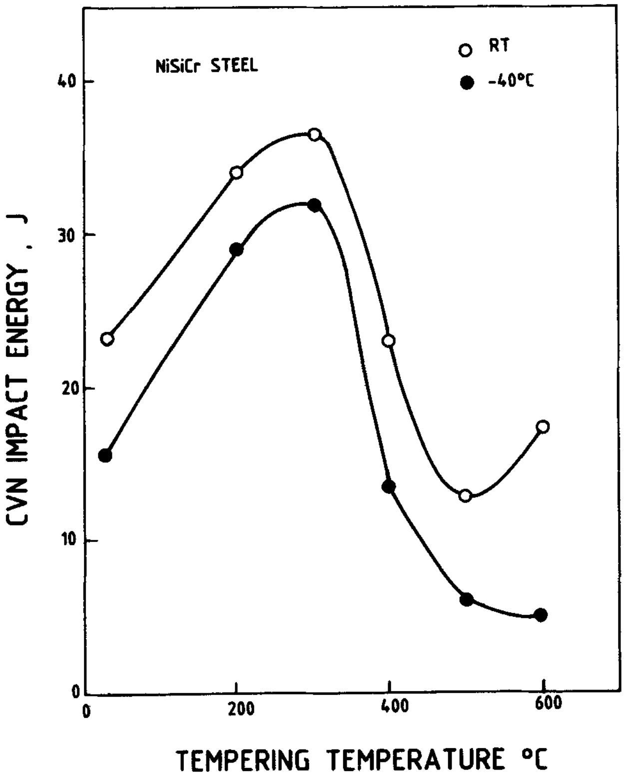

Figure 4. CVN impact energy as a function of tempering temperature for NiSiCr steel.

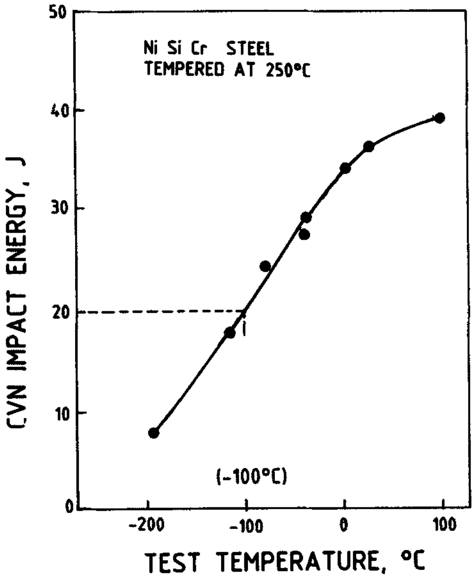

Figure 5. CVN impact energy as a function of test temperature for NiSiCr steel.

250°C-tempered condition is plotted against test temperature in figure 5. The 20 J criterion yields a DBTT of $-100°C$. Mechanical properties of the base Garrison NiSiCr steel subjected to an optimum treatment of 250°C tempering are summarized in table 2.

Based on the understanding developed through the basic studies described in the preceding section, cobalt addition was made to the base Garrison NiSiCr steel to achieve further improvement in fracture toughness. The tempering behaviour of NiSiCrCo steel is shown in figures 6 and 7. The variation of strength with tempering temperature, given in figure 6, shows that yield strength increases with increasing tempering temperature, reaching a maximum at 250°C. Further increase in tempering

Table 2. Mechanical properties of steels developed in the present study in the 250°C-tempered condition.

Material	YS (MPa)	UTS (MPa)	RA (%)	CVN impact energy at RT (J)	K_{IC} (MPa$\sqrt{m}$)
NiSiCr	1550	1825	47	36	103
NiSiCrCo	1360	1670	50	52	140
NiSiCrMo	1648	1904	48	35	102
NiSiCrCoMo	1530	1890	48	34	120

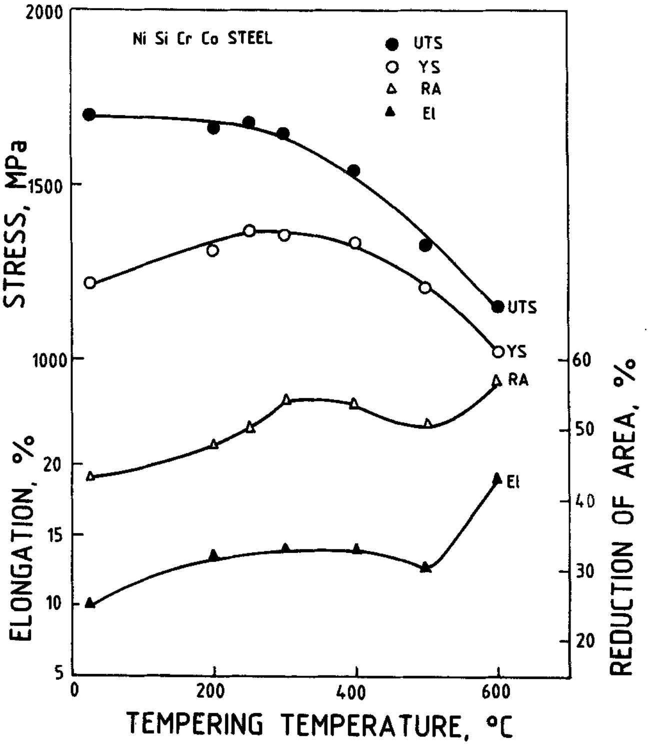

Figure 6. Tensile properties of NiSiCrCo steel as a function of tempering temperature.

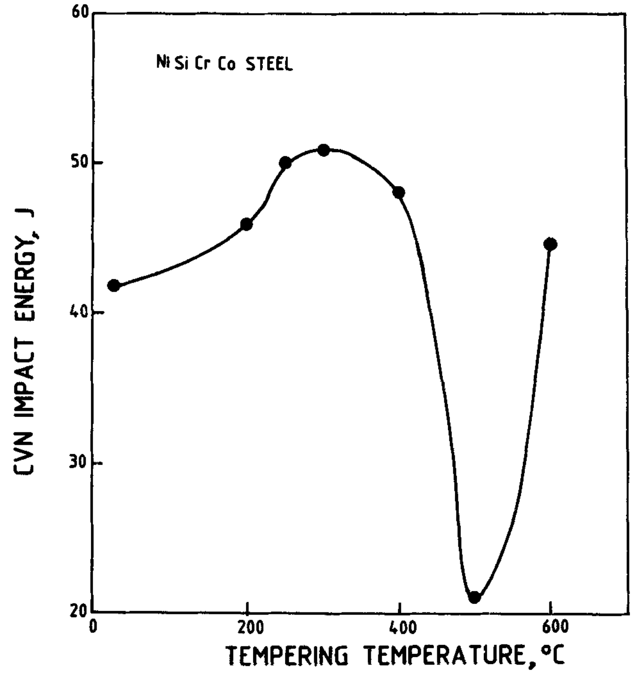

Figure 7. CVN impact energy at room temperature as a function of tempering temperature for NiSiCrCo steel.

temperature decreases the yield strength. On the other hand, ultimate tensile strength remained nearly constant up to tempering temperature of 300°C, beyond which it decreased with increasing tempering temperature. Ductility (elongation and reduction in area) shows a trough in the tempering temperature range 400 to 500°C. It is seen from figures 6 and 7 that NiSiCrCo steel develops an optimum combination of strength and impact toughness in the 250°C-tempered condition. Fracture toughness tests carried out in this optimum condition yielded a K_{IC} value of 140 MPa$\sqrt{m}$. The impact toughness in the 250°C-tempered condition is plotted against test temperature in figure 8. The 20 J criterion yields a DBTT of − 150°C. Mechanical properties of the NiSiCrCo steel subjected to an optimum treatment of 250°C tempering are included in table 2. A significant increase in fracture toughness is seen with an accompanying loss in strength. However, the loss in strength is not in proportion to the increase in fracture toughness. A 40% increase in fracture toughness is seen while the loss in strength is around 10% (table 2). It is also seen from figures 3 and 6 that the strength of NiSiCrCo steel is lower than that of the base Garrison steel at all tempering temperatures.

The increase in fracture toughness with an accompanying loss in strength with cobalt addition to base steel is in line with the observations made on cobalt addition to Armco iron (Srinivas *et al* 1988, 1993). Microsegregation studies carried out on NiSiCrCo steel using a scanning Auger microscope show segregation of carbon to grain boundaries (figure 9). The increase in fracture toughness with cobalt addition is attributable to the segregation of carbon to the grain boundaries, thus increasing the cohesive strength of the grain boundary and rendering the crack initiation process that much more difficult (Olson 1990; Misra and Rama Rao 1993).

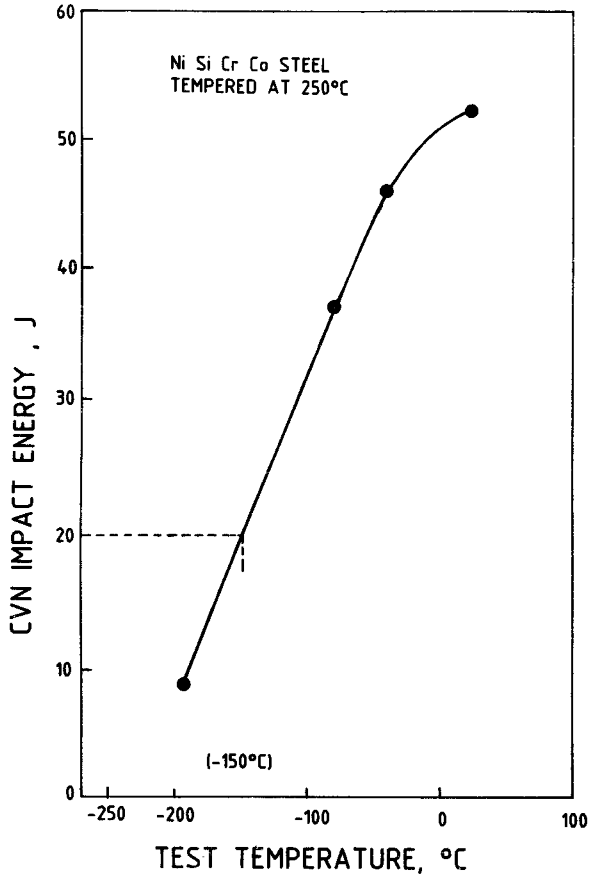

Figure 8. CVN impact energy as a function of test temperature for NiSiCrCo steel tempered at 250°C.

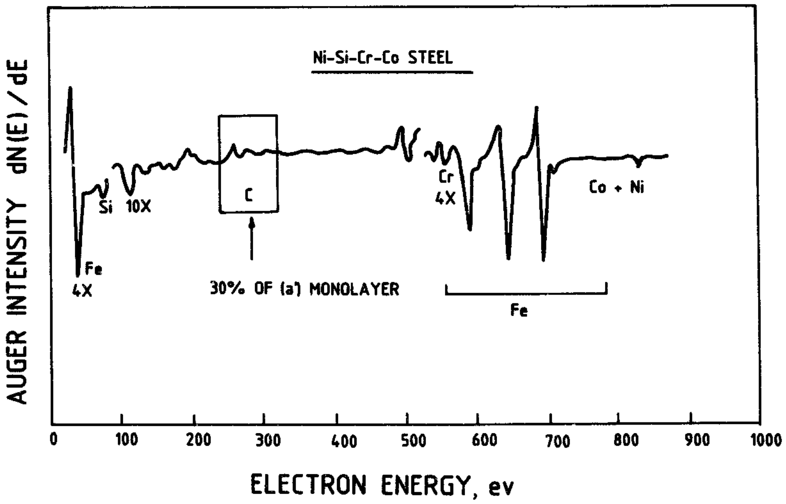

Figure 9. Scanning Auger spectrum showing carbon segregation at grain boundaries in NiSiCrCo steel.

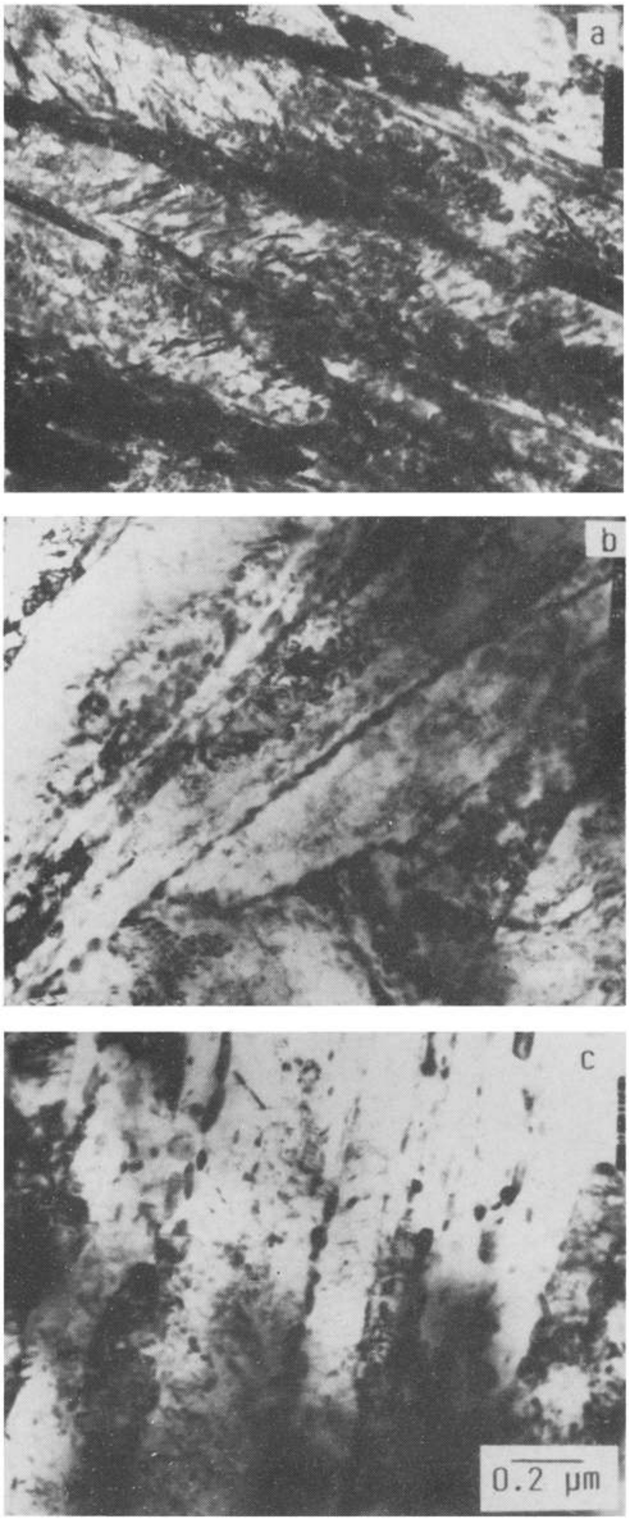

Figure 10. TEM micrographs of NiSiCr steel tempered at (**a**) 250°C and (**b**) 500°C, showing interlath-retained austenite and carbide stringers respectively. (**c**) Coarse interlath carbides are shown in the 600°C-tempered condition.

Comparison of data in figures 4 and 7 reveals that cobalt addition to NiSiCr steel significantly improves the impact toughness at all tempering temperatures. It is to be noted that though the trough in the impact toughness still prevails, with a minimum value at 500°C tempering temperature, the lowest observed value for the NiSiCrCo steel is nearly twice as large as that for the NiSiCr steel.

The loss in ductility and impact toughness when tempered in the temperature range 350 to 600°C suggests occurrence of embrittlement. It is now well established that tempered martensite embrittlement (TME) occurs in low-alloy steels when tempered in the temperature range 250 to 400°C (Sarikaya *et al* 1983; Zia-Ebrahimi and Krauss 1983, 1984; Bandyopadhyay and McMahon 1983; Briant 1989; Darwish *et al* 1991). Silicon is known to shift TME to higher temperatures (Barnard *et al* 1982). Transmission electron microscopy carried out on 250°C-, 500°C- and 600°C-tempered specimens of base Garrison NiSiCr steel revealed the presence of interlath-retained austenite in the 250°C-tempered condition (figure 10a) and transformation of retained austenite to carbides in the 500°C-tempered condition (figure 10b). Coarse interlath

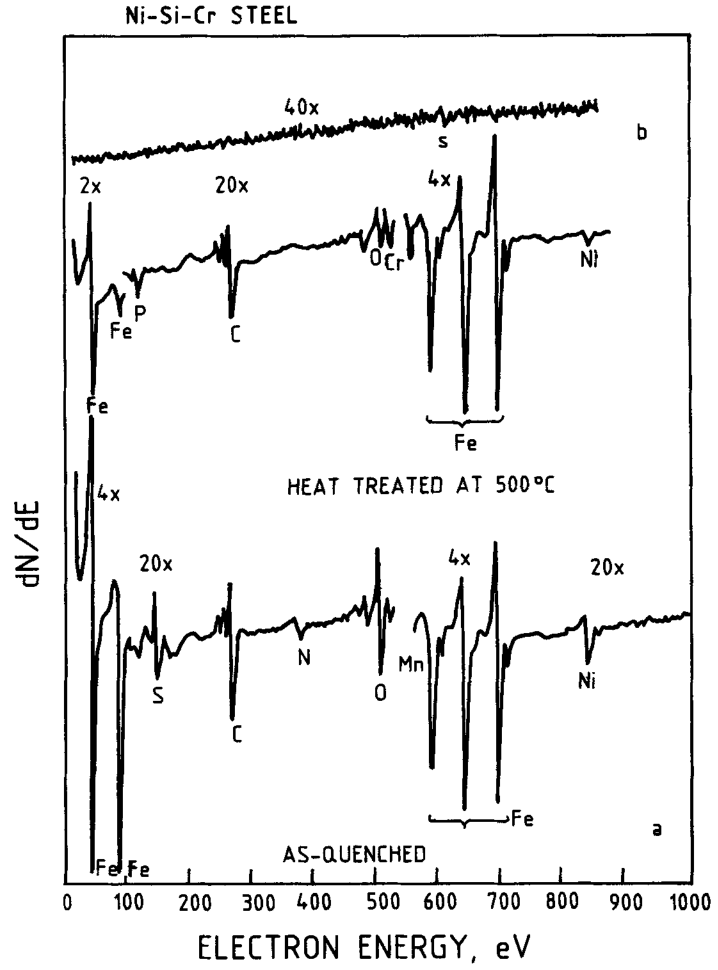

Figure 11. Auger spectra for NiSiCr steel (**a**) as-quenched and (**b**) 500°C-tempered condition.

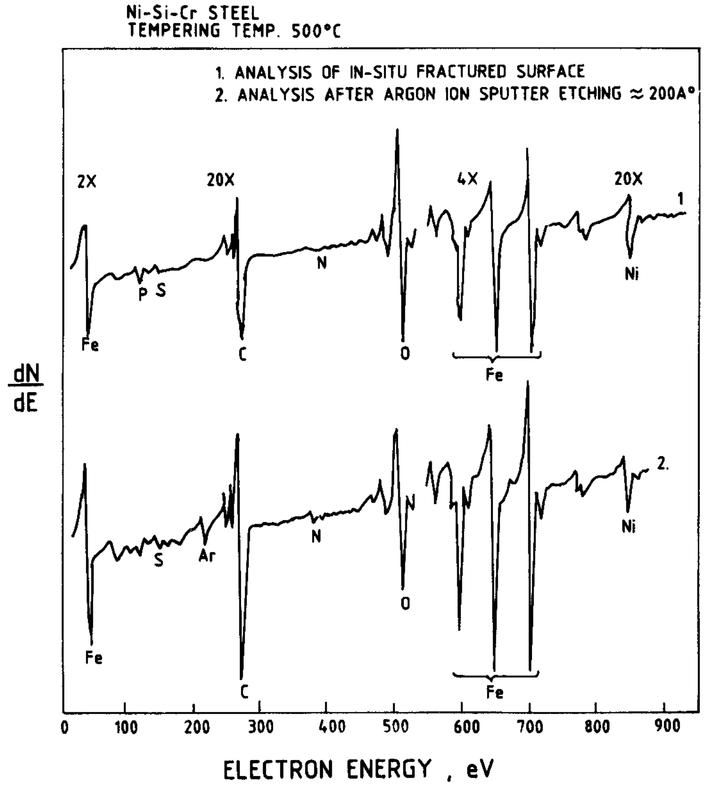

Figure 12. Auger spectra revealing absence of P peak after sputter etching to a depth of around 200 Å in NiSiCr steel tempered at 500°C.

carbides are seen in the 600°C-tempered condition (figure 10c). These observations suggest occurrence of TME in the temperature range 300 to 600°C. Further, Auger electron spectroscopy carried out on 500°C-tempered specimen provided evidence of temper embrittlement (TE). As quenched, as well as 500°C-tempered specimens, were fractured *in situ*. Auger spectra, given in figure 11, show segregation of phosphorus in the 500°C-tempered condition while the same is absent in the as-quenched condition. Sputter etching of the fractured surface by argon ions up to a depth of around 200 Å resulted in the absence of the P peak (figure 12), reflecting the fact that phosphorus segregation was confined to a thin grain boundary layer. TEM and AES studies therefore suggest that the loss in ductility and impact toughness in the temperature range 300 to 600°C is due to the simultaneous occurrence of TME and TE.

To build up strength in the presence of cobalt in the base NiSiCr steel, molybdenum addition was resorted to. We have shown (table 1) that while molybdenum is a solid solution strengthener in iron, the fracture toughness of Armco iron is only marginally lowered as a result of molybdenum addition. The influence of molybdenum on the base composition of Ni–Si–Cr steel was therefore studied. The mechanical properties and the fracture toughness of NiSiCrMo steel in the 250°C-tempered condition are given in table 2. Compared to the properties of the base Garrison steel an increase in yield and ultimate tensile strength with negligible reduction in fracture toughness

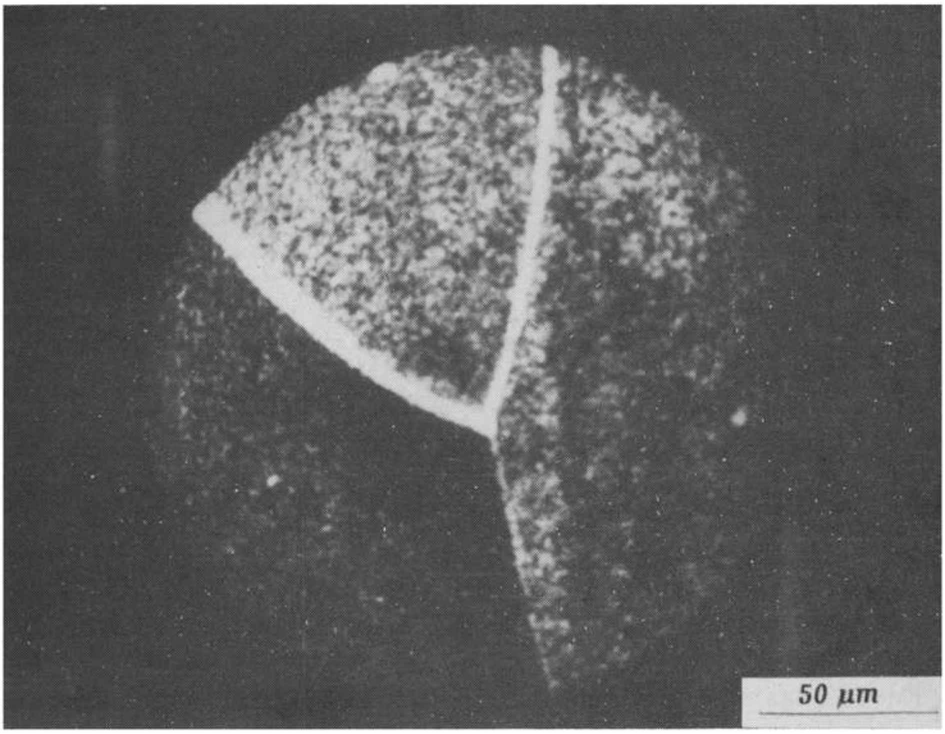

Figure 13. SIMS ion image showing carbon segregation to grain boundaries in NiSiCrCoMo steel.

was observed. The increase in yield strength is as much as 7% while the increase in UTS is around 5%.

With the understanding thus developed, molybdenum addition was made to the cobalt-containing steel. To optimize the composition further, melts with varying content of cobalt and molybdenum were taken and processed. The tempering behaviour of each steel was studied and the optimum property combination was established.

The mechanical properties and fracture toughness of the optimized NiSiCrCoMo steel are also given in table 2. The fracture toughness of NiSiCrCoMo steel is nearly 15% higher than that of base Garrison NiSiCr steel at a matching strength level. Secondary ion mass spectroscopy studies carried out on the optimized steel composition revealed carbon segregation to grain boundaries (figure 13). With these observations of higher fracture toughness and carbon segregation in cobalt-containing NiSiCrMo steel, the view that grain boundary carbon, which enhances grain boundary cohesion, can contribute to higher fracture toughness (Olson 1990; Misra and Rama Rao 1993) is reiterated.

3.3 *Reproducibility on tonnage scale*

Two 5 ton capacity melts of NiSiCrCoMo steel were taken and processed by Mishra Dhatu Nigam Limited (MIDHANI), a public sector undertaking. Electric arc steel melting, followed by vacuum arc refining process, was employed. The mechanical properties of NiSiCrCoMo steel processed on this scale are given in table 3 and compared with those derived from a laboratory-scale melt. The attractive combination of strength and toughness observed in the laboratory melt is clearly reproduced in the industrial-scale melt.

3.4 *Comparison with other ultra-high-strength steels*

The properties of NiSiCr, NiSiCrCo, NiSiCrMo and NiSiCrCoMo steels are compared in figure 14 with those of the low-alloy steels AISI 4340, 15CDV6 and D6ac, and highly alloyed HP 9-4-30 and maraging steels. While the strength–toughness combination of the base Garrison NiSiCr steel is quite comparable to that of D6ac steel, the cobalt- and molybdenum-containing (NiSiCrCoMo) steel possesses properties superior to 15CDV6 and D6ac steels. The strength–toughness data for NiSiCrCo and

Table 3. Mechanical properties of NiSiCrCoMo steel.

Property	Lab-scale melt	Industrial-scale melt*
YS (MPa)	1530	1670–1750
UTS (MPa)	1890	1930–1980
El (25 mm GL) (%)	14	11–13
RA (%)	48	43–46
CVN impact energy at RT (J)	34	28–32
K_{IC}(MPa$\sqrt{m}$)	120	90–110

*The property range is due to the properties obtained at various stages of processing of the ingot to hot-formed products.

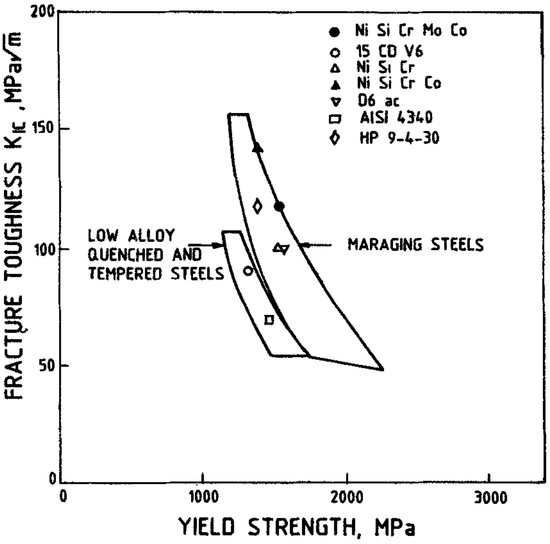

Figure 14. Fracture toughness vs yield strength for various ultra-high-strength steels.

NiSiCrCoMo steels fall in the upper bound range for 250-grade maraging steel. The newly developed NiSiCrCoMo steel obviously provides significant cost saving once we consider the fact that this steel possesses a maximum alloy content of ~7% whereas the alloying content of maraging 250-grade steel is in excess of 30%. NiSiCrCoMo steel is an inexpensive and therefore an attractive substitute for the maraging. steel.

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