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Effect of alloying additions on K_{ISCC} of ultrahigh strength NiSiCr steel

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Abstract. The effect of alloying additions viz. cobalt, molybdenum, cerium and a combination of cobalt and molybdenum, on the K_{ISCC} of NiSiCr steel in 3·5% NaCl aqueous solution was studied. Addition of cobalt to NiSiCr steel resulted in an increase in the K_{ISCC} whereas molybdenum addition decreased the K_{ISCC}. Cerium addition did not affect the K_{ISCC} while the combination of cobalt and molybdenum resulted in an increase in the K_{ISCC} although not as much as in the case of cobalt addition. The effect of alloying elements on K_{ISCC} could be attributed to their effect on the critical fracture stress and yield strength.

Keywords. Ultrahigh strength steels; fracture toughness; threshold stress intensity for stress corrosion cracking, K_{ISCC}; segregation.

1. Introduction

In recent years, much attention has been given to the development of ultrahigh strength steels for critical aerospace and marine applications requiring high specific properties (Garrison 1990; Tomita 1991). Garrison (1986) developed a NiSiCr steel with a good combination of strength and fracture toughness. Recent studies on the influence of alloying elements on fracture toughness of iron (Srinivas *et al* 1994) have shown that the addition of cobalt significantly enhances the fracture toughness of iron while the addition of Mo, Ni or Si decreases the same in that order. Malakondaiah *et al* (1994) showed that the addition of Co to NiSiCr steel improves the fracture toughness considerably whereas the addition of molybdenum reduces the same slightly. The beneficial effect of rare earth additions has been discussed by Garrison and Handerhan (1990).

Ultrahigh strength steels are susceptible to stress corrosion cracking in aqueous solutions (Proctor and Paxten 1969; Gerberich and Chen 1975; Waid and Ault 1976; Li *et al* 1992). Fracture mechanics principles and precracked specimens have been used to advantage in the last few years in evaluating the stress corrosion cracking resistance of metallic alloys (Hyatt 1970; Hauser *et al* 1974; Kaufman *et al* 1976; ASM Metals Handbook 1987). The characterizing parameter in this approach is the threshold stress intensity factor (K_{ISCC}), below which the crack propagation rates are vanishingly small. The objective of the present study was to investigate the effect of alloying additions, viz. Co, Mo, a combination of Mo and Co and Ce, on the K_{ISCC} of NiSiCr steel in 3·5% NaCl aqueous solution.

2. Experimental

The nominal composition in wt.% of the base NiSiCr steel was 0·34 C, 3 Ni, 2 Si and 1 Cr. Small amounts (< 1%) of Co, Mo, Ce or combination of Co and Mo were added to the base steel to study the effect of alloying additions. All the steels except NiSiCr + Co + Mo were vacuum induction melted. NiSiCr + Co + Mo steel was produced by air induction melting followed by vacuum arc refining (VAR) and had relatively higher C (0·37). Specimen blanks were quenched from 1173 K and tempered at 523 K. The tensile properties and fracture toughness were evaluated in the longitudinal and L–T orientation, in accordance with, respectively, ASTM E-8 (1991) and ASTM E-399 (1991).

Compact tension specimens (see figure 1) with $W = 50{\cdot}8$ mm, $B = 4$ mm and $a = 25{\cdot}4$ mm were used for evaluating the K_{ISCC} utilizing the proof ring load method. The experimental details of this technique are available in Kaufman *et al* (1976). The compact tension specimen was immersed in a 3·5% NaCl aqueous solution which was constantly circulated by means of a pump. 150 h at a given stress intensity factor without crack extension was chosen as the criterion for the estimation of K_{ISCC}. For all compositions, the stress intensity factor was increased by increments of 0·5 MPa$\sqrt{m}$ until crack initiation occurred within the 150 h period. The highest stress intensity factor where crack extension did not occur in 150 h was considered as K_{ISCC}. The crack initiation was determined with the help of a previously calibrated LVDT. However, the crack propagation behaviour (da/dt vs K) could not be determined as the crack propagation rate in all the specimens was

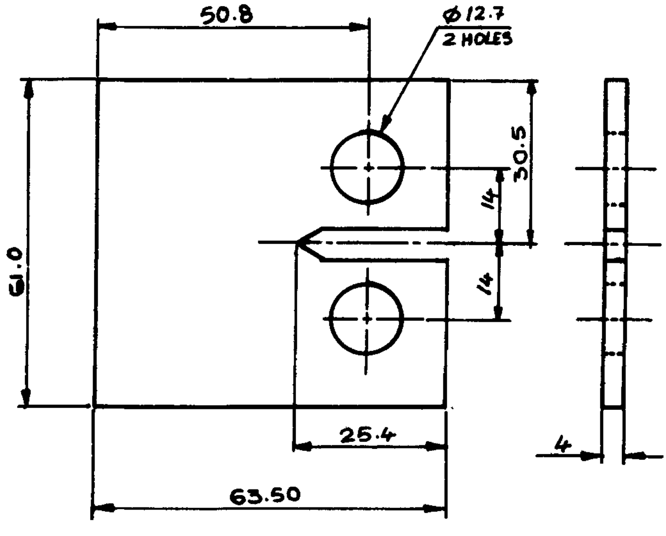

Figure 1. Compact tension specimen geometry used for K_{ISCC} evaluation (all dimensions are in mm).

extremely rapid. A minimum of two tests were carried out in each case. The fractured surfaces were examined in an SEM to study the mode of fracture. Electron probe microanalysis (EPMA) and secondary ion mass spectroscopy (SIMS) were carried out to study the segregation of elements at the prior austenitic grain boundaries.

3. Results

The tensile properties and fracture toughness of the steels investigated are presented in table 1. It is evident from table 1 that the addition of Co decreases the yield strength and increases the fracture toughness of the base steel (NiSiCr), while Mo addition increases the yield strength and marginally decreases the fracture toughness of the base steel. Ce addition has no influence on either the yield strength or fracture toughness while a combination of Co and Mo results in an increase in both yield strength and fracture toughness. The K_{ISCC} values are also given in table 1. The values listed are an average of two tests with the mean spread of the two values being less than 1 MPa$\sqrt{m}$ in all cases. The trend in the K_{ISCC} values (see table 1) is similar to that seen for K_{IC} with Co and Co + Mo additions resulting in an increase, Mo addition resulting in a decrease and Ce addition resulting in no change in the K_{ISCC} of the base steel.

Representative EPMA carbon element maps for NiSiCr steel and NiSiCr steel with Co addition are shown in figures 2a and b, respectively. Figure 2 reveals that there is no preferential segregation of carbon at the prior austenitic grain boundaries in the case of NiSiCr steel while there is a significant carbon segregation at the prior austenitic grain boundaries in the case of NiSiCr + Co steel. NiSiCr + Ce and NiSiCr + Mo steels exhibit a behaviour similar to that seen in NiSiCr steel whereas NiSiCr + Co + Mo steel shows, again, carbon segregation at the prior austenitic grain boundaries. Representative SIMS ion images for NiSiCr + Co + Mo steel and NiSiCr + Mo steel are shown in figures 3a and b, respectively. Figure 3a clearly reveals the segregation of carbon at the prior austenitic grain boundaries, while figure 3b shows the absence of such behaviour substantiating the EPMA observations.

SEM fractographs for NiSiCr, NiSiCr + Mo and NiSiCr + Co steels are shown in figures 4a,b and c, respectively. Figures 4a and b are representative of NiSiCr + Ce steel whereas figure 4c is representative of NiSiCr + Co + Mo steel. It is evident from the SEM fractographs that the fracture mode is intergranular in NiSiCr,

Table 1. Tensile, fracture toughness and stress corrosion properties of steels investigated.

Material	σ_{ys} (MPa)	K_{IC} (MPa$\sqrt{m}$)	K_{ISCC} (MPa$\sqrt{m}$)
NiSiCr	1550	103	18
NiSiCr + Ce	1550	102	19
NiSiCr + Mo	1648	100	15
NiSiCr + Co	1360	140	25
NiSiCr + Co + Mo	1670	110	22

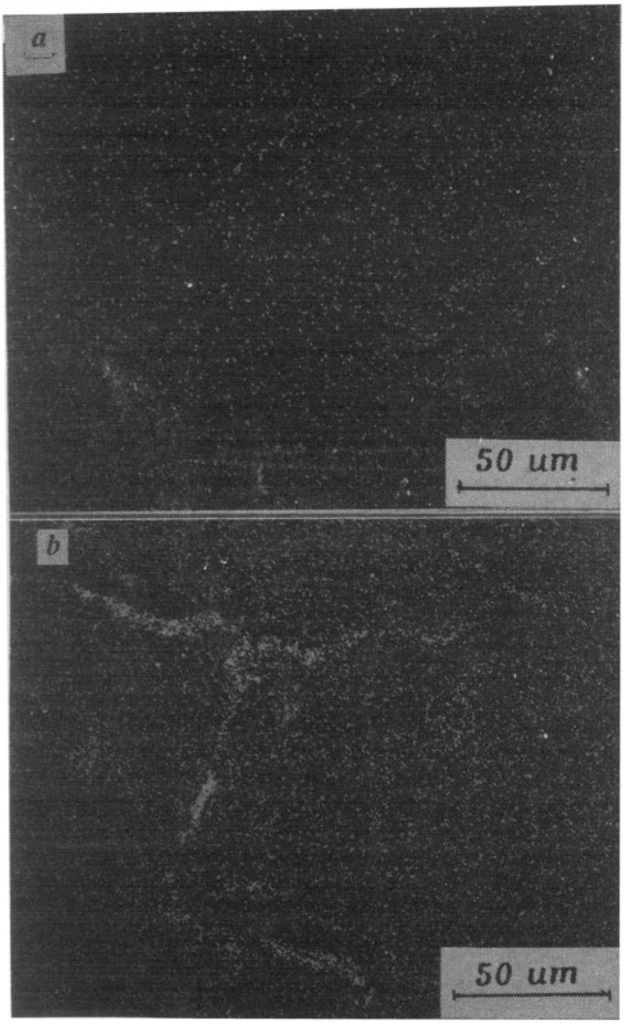

Figure 2. Representative carbon element map obtained from EPMA for (a) NiSiCr and (b) NiSiCr + Co steel.

NiSiCr + Mo and NiSiCr + Ce steel while it is predominantly transgranular in NiSiCr + Co and NiSiCr + Co + Mo steels.

4. Discussion

In the existing threshold models (Orian and Josephic 1974, 1977; Doig and Jones 1977; Gerberich and Wright 1981) for stress corrosion cracking the hydrostatic stress elevation in the near crack tip region is presumed to cause local hydrogen accumulation and fracture is said to result when the local maximum tensile stress from the applied loading exceeds the local fracture stress (a material property). The hydrogen accumulation is responsible in the sense that it causes the local fracture stress to drop below the local crack tip tensile stress. Nair and Tien (1985)

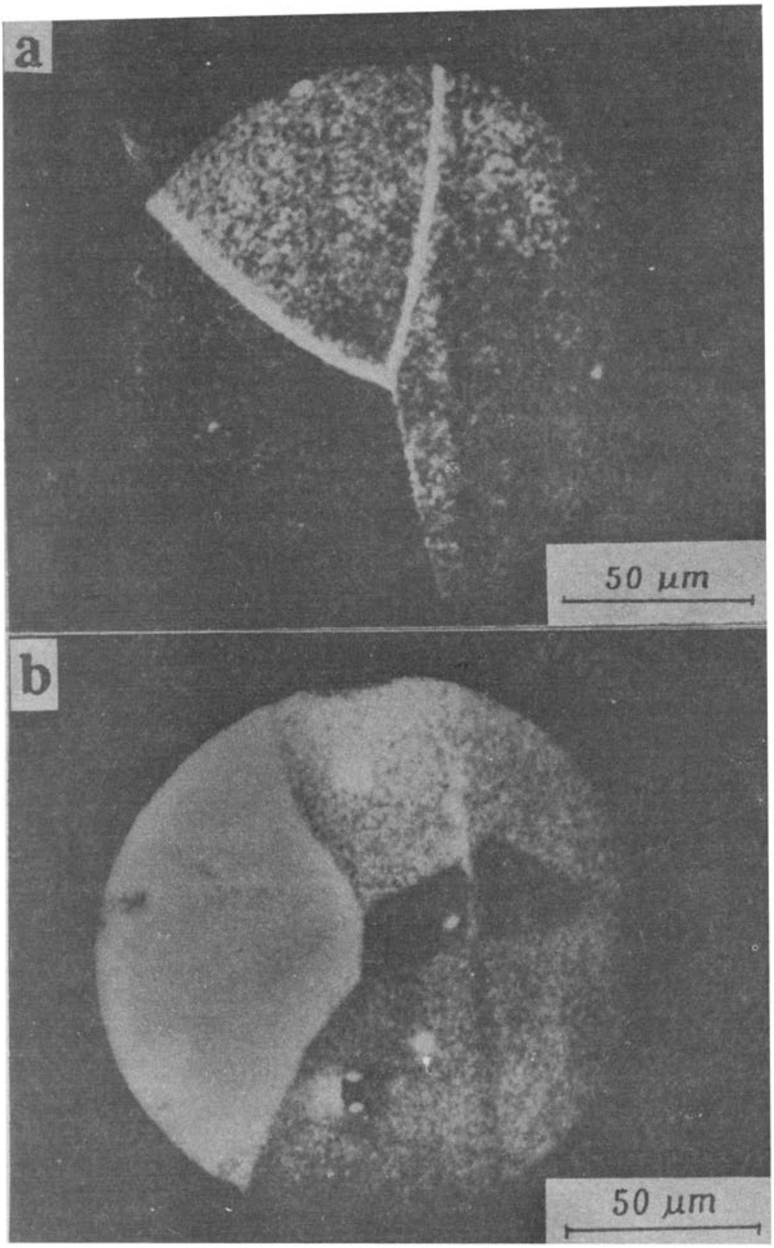

Figure 3. SIMS ion images illustrating (**a**) segregation of carbon at prior austenitic grain boundaries in NiSiCr + Mo + Co steel and (**b**) absence of carbon segregation in NiSiCr + Mo steel.

suggested that the tensile stress elevation in the near crack tip region is not a sufficient condition for fracture initiation to occur. The local flow stress in the crack tip plastic zone must exceed the critical value over a critical distance related to some microstructural weak link. According to this model, the variation in K_{ISCC} with alloying addition could be attributed to essentially two factors i.e. variation

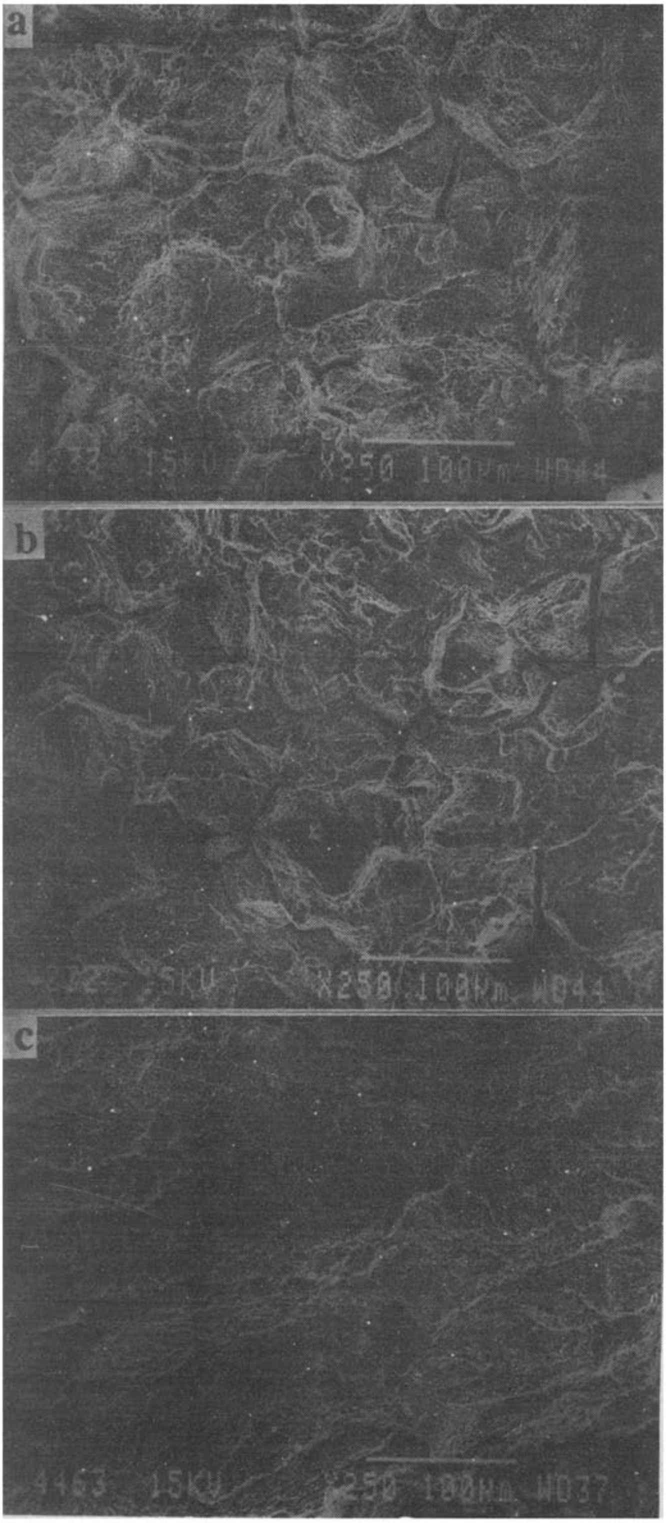

Figure 4. Representative SEM fractographs showing intergranular fracture mode in **(a)** NiSiCr steel, **(b)** NiSiCr + Mo steel and **(c)** transgranular fracture mode in NiSiCr + Co steel.

in (i) yield strength and (ii) critical fracture stress. An increase in yield strength results in an increase in the local crack tip flow stress causing critical fracture stress to be reached at a lower applied stress intensity factor K_{ISCC}. On the other hand, an increase in the critical fracture stress, which is proportional to the cohesive strength of the grain boundary, results in a requirement of a higher applied stress intensity factor for fracture to occur.

Cobalt addition to the base NiSiCr steel results in the preferential segregation of carbon to the prior austenitic grain boundaries (figures 2b and 3a). It is known that segregation of carbon to the prior austenitic grain boundaries can cause an enhancement in grain boundary cohesion (Seah 1980; Messemer and Briant 1982; Seah and Hondrous 1983; Hansen and Grabke 1986; Suzuki *et al* 1987; Olson 1990; McMahon Jr. 1991). The reason for the improvement in grain boundary cohesion with carbon segregation in iron base alloys is two-fold. One effect is to displace harmful impurities, like *P* (Misra and Rama Rao 1993) and *S* (Shin and Tsao 1988; Misra and Rama Rao 1993), from grain boundaries due to the high free energy of carbon segregation to grain boundaries (ΔG_B°) as compared to that of the other segregants and thereby reduce the detrimental effect of these impurities. Secondly, segregation of carbon at the grain boundaries in iron-base alloys per se promotes cohesion in the manner elucidated recently by Rice and Wang (1989). The increase in grain boundary cohesion gives rise to an increase in the critical fracture stress as is reflected in the observation of higher energy transgranular fracture in the fracture surface (figure 4c). The addition of Co also results in lowering of the yield strength. Thus, as discussed earlier, both the factors contribute to a higher K_{ISCC} in NiSiCr + Co steel. In the case of NiSiCr + Mo steel, there is an increase in the yield strength as compared to the NiSiCr steel and no observable change in the segregation of carbon atoms to the prior austenitic grain boundaries (figures 2a and 3b). Thus, the lower K_{ISCC} in this case can be explained solely on the basis of the increase in yield strength because of which the local crack tip flow stress attains the critical fracture stress at a lower applied stress intensity factor (K_{ISCC}). In the case of NiSiCr + Co + Mo steel, the yield strength is higher than that of the base steel but there occurs also preferential segregation of carbon to the prior austenitic grain boundaries (figures 2b and 3a). The higher yield strength results in a lowering of the K_{ISCC} but this is more than compensated for by the increase in σ_f^+ as a result of carbon segregation to the grain boundaries. The net effect is an increase in K_{ISCC}. Thus, the NiSiCr + Co + Mo steel exhibits higher K_{ISCC} than the base steel but a lower K_{ISCC} than the NiSiCr steel with only Co addition. In the case of cerium addition to NiSiCr steel, there is neither a change in the yield strength nor the segregation pattern of carbon. This is also reflected in the K_{ISCC} value being nearly the same as that of NiSiCr steel.

An important goal in material design is to maximize K_{ISCC} and K_{IC} without undue loss in the yield strength. The variation of K_{ISCC} and K_{IC} with σ_{ys}, for NiSiCr based steels is shown in figure 5. The figure shows that both K_{ISCC} and K_{IC} decrease with increasing yield strength. The best combination of K_{ISCC} and K_{IC} are observed in the steel with Co addition. However, this is achieved at the cost of a significant loss in yield strength. On the other hand, the addition of Co and Mo together results in an improvement in K_{ISCC}, K_{IC} as well as yield strength. This is best illustrated in the form of variation of the product of K_{ISCC} and K_{IC} with σ_{ys} as shown in figure 6. This figure also includes the data for a few other ultrahigh

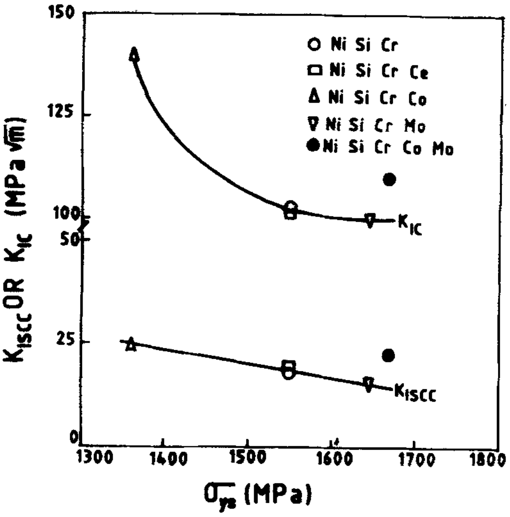

Figure 5. Variation of K_{ISCC} and K_{IC} with yield strength for the NiSiCr based steels.

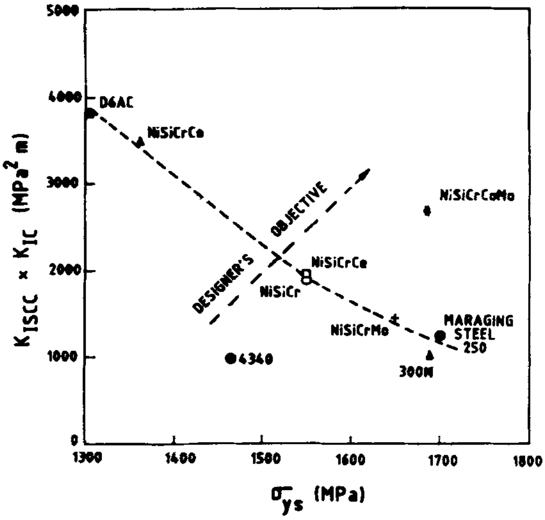

Figure 6. Variation of the product of K_{IC} and K_{ISCC} with yield strength for the NiSiCr based and other ultrahigh strength steels.

strength steels, D6AC, 4340, maraging steel 250 and 300 M steel. Compared to all of these, it is concluded that NiSiCr + Co + Mo steel possesses superior property combination.

5. Conclusions

(i) Cobalt, molybdenum and cerium addition increases, decreases and does not change the K_{ISCC} of NiSiCr steel, respectively. A combination of Co and Mo additions, however, results in an improvement in the K_{ISCC} of NiSiCr steel although not as much as in the case of only cobalt addition.

(ii) The effect of alloying additions on K_{ISCC} of NiSiCr steel can be explained on the basis of Nair and Tien's plastic flow model for K_{ISCC}.

(iii) A superior combination of K_{ISCC}, K_{IC} and yield strength is achieved for NiSiCr steel alloyed with Co + Mo.

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