An ad-hoc committee selected the following paper--"Grain Boundary Embrittlement by μ and σ Phases in Iron-Base Superalloys"--as the BEST PAPER submitted to this International Symposium. The decision was based on such criteria as industrial pertinence, long-term impact, originality and thoroughness of research.

GRAIN BOUNDARY EMBRITTLEMENT BY μ AND σ PHASES IN IRON-BASE SUPERALLOYS

Guolian Chen,* Xishan Xie,* Kequan Ni, Zhichao Xu and
Di Wang
Beijing University of Iron and Steel Technology
Beijing, China

Ming Zhang
Shanghai Iron and Steel Research Institute
Shanghai, China

Yuying Ju
Shanghai Fifth Steel Plant
Shanghai, China

Grain boundary embrittlement by μ and σ phases was studied in 15Cr/25Ni and 15Cr/40Ni type iron-base superalloys. The embrittlement of iron-base superalloys can be sensitive to small amounts of μ and σ phases present at the grain boundaries, even when the weight fraction is between 0.01 and 1%. The degree of embrittlement was found to be directly proportional to the concentration coefficients of the μ and σ phases at the grain boundaries. The embrittlement effect results in intergranular fracture during impact testing. Fracture mechanisms caused by the μ and σ phases were quite different. This embrittlement effect was suppressed by reducing the grain size or by decreasing or removing the grain boundary embrittling μ and σ phases by controlling the chemical compositions of the alloys.

INTRODUCTION

In the review papers of Sullivan (1), Decker (2), Sims (3) and Sabal et al. (4), it was shown that precipitation of minor intermetallic phases such as σ , Laves, G and μ phase can in-

---

* Professor Guolian Chen and Professor Xishan Xie are presently Visiting Scholars, Columbia University, New York, NY 10027

fluence mechanical properties. Many researchers (5,6,7,8) have studied the embrittling effect of σ platelets precipitated in great amounts (usually about 2-5%) inside the grains of superalloys. However, it appears little is documented on the embrittling effects of equiaxed σ phase precipitated in small amounts at the grain boundaries of superalloys.

As for the effect of μ phase, little information has been published with respect to its effects on the iron-base superalloys. The precipitation of intragranular μ platelets in the iron-base superalloy Incoloy 901* after 1000 hrs aging at different temperatures between 760° and 927°C was first identified by Beattie and Hagel (9). Subsequently, Maniar *et al.* (10) studied μ phase precipitation during aging between 649° and 760°C in Pyromet 860,* and Wood (11) studied μ phase precipitation during long-time stress rupture in D979 at temperatures between 538° and 816°C. These investigations did not pursue the systematic relationship between μ phase precipitation and mechanical properties, but in Maniar *et al.*'s paper it was mentioned that the formation of μ phase in Pyromet 860 did not apparently affect the mechanical properties.

In contrast to these earlier studies, this investigation was undertaken to study embrittlement caused by small amounts of equiaxed σ or μ phases precipitated at the grain boundary. From the results it appears that it would be very important to assess this embrittlement effect if a long-time service of the iron-base superalloys at the 650°-750°C range is required.

EXPERIMENTAL PROCEDURE

Two types of alloys were used, the nominal chemical compositions of which are shown in Table I.

Table I. Nominal Chemical Compositions (wt.%)

Type of Alloys	Wrought bar diameter	Chemical Composition							
		C	Cr	Ni	W	Mo	Al	Ti	B
15Cr/25Ni	φ18mm	0.05	15	25	-	1.25	0.3	2	0.006
15Cr/40Ni	φ18mm	0.05	15	40	4	2	2	2.5	0.006

*Incoloy and Pyromet alloys are trademark alloys of the International Nickel Company and Carpenter Technology Corporation, respectively.

The 15Cr/25Ni type iron-base superalloys were studied for embrittlement by the σ phase. All samples of these alloys were first given a heat treatment of 980°C/1hr/oil quench and 720°C/16hr/air cool. Based on results obtained by applying PHACOMP to the iron-base superalloys (12), i.e., $\Delta N_V' = \text{Ni}-3\text{Ti}-3.5\text{Al}-1.7\text{Si}-0.9\text{Cr}-4.7$, when $\Delta N_V' > 0$, the alloy should remain σ free. The amount of σ phase was changed by varying the Ni (from 24-27%) and Cr (from 14-17%) content in some experimental heats, which were exposed to 650°C for 1600 hrs. Alternatively, different amounts of σ phase were obtained in a 15Cr/25Ni type alloy by increasing the exposure time at 650°C up to 6000 hrs.

The effect of μ phase formation was studied in the 15Cr/40Ni type alloys. Different amounts of μ phase were obtained by: (1) exposing specimens at 700°C, 750°C for 10,000 hrs, and at 800°C for 1000 hrs, after administering a heat treatment of 1180°C/2hrs/A.C. + 1050°C/4hrs/A.C. + 800°C/16hrs/A.C.; or (2) choosing different aging parameters on the basis of the kinetics of precipitation of the μ phase (13), that is 700°C, 800°C or 900°C/16hrs/A.C. + 700°C/16hrs/A.C., 900°C/16hrs/A.C. + 700°C/1000hrs/A.C., or 800°C/200hrs/A.C. + 700°C/16hrs/A.C., after administering a solid solution treatment of 1140°C/2hrs/A.C. These special heat treatments were designed for the formation of μ phase primarily at grain boundaries.

The mechanical properties of these alloys were studied through tension tests and impact tests at ambient temperature and at 650°C for the 15Cr/25Ni type alloys and at ambient temperature and 750°C for the 15Cr/45Ni alloys, and by performing stress rupture tests at 650°C and 750°C for 15Cr/25Ni and 15Cr/40Ni alloys, respectively.

The phase identification, morphology determination, quantitative metallography of μ and σ phases were done using optical and electron microscopes, x-ray and electron diffractions, electron and ion microprobe analyses. The wt.% of σ and μ was determined by chemical analyses after electrolytic extractions (13,14). The fracture surfaces were also examined in the scanning electron microscope.

RESULTS AND DISCUSSION

The Embrittlement Effect of σ and μ Phase

The embrittlement effect caused by the precipitation of σ phase at grain boundaries (see Foto.1) after long-time ex-

5μ

Foto 1. An example of grain-boundary α phase precipitated after long-time exposure at 650°C in 15Cr/25Ni type alloy

10μ

Foto 2. An example of α phase precipitated after long-time exposure in 15Cr/40Ni alloy

10μ

5μ

Foto 3. The influence of grain boundary α phase on fracture in 15Cr/40Ni type alloy. (a) Intragranular fracture--no α phase

20μ

5μ

Foto 3. (b) Intra- and intergranular fracture--small amount of grain boundary α phase

20μ

5μ

Foto 3. (c) Intergranular fracture--great amount of grain boundary α phase

10μ

Foto 4. A typical intergranular dimple fracture in a 15Cr/25Ni type alloy after long-time exposure at 650°C

3μ

Foto 5. (a) Higher magnification of the 15Cr/25Ni type alloy fracture surface showing α phase particles in the dimples and (b) the x-ray spectrum of a FeCr α -phase particle

Foto 6. A typical low ductile intergranular fracture surface in a 15Cr/40Ni type alloy with phase precipitated at grain boundary α phase

Foto 7. Higher magnification of the 15Cr/40Ni type alloy fracture surface showing the protruding grain boundary α phase

posures up to 6000 hrs at 650°C for one 15Cr/25Ni type alloy is shown in Fig. 1. The ambient temperature impact toughness of this alloy is seen to decrease from about 10 to 5 kgm/cm² when σ phase is present at the very small amount of about 0.02%, and it reduces further to 2 kgm/cm² when the amount of σ phase increases to about 0.6%. Fig. 2 shows the embrittling effect of σ phase in several 15Cr/25Ni type alloys with varying Ni and Cr contents, each of which was exposed to 650°C for 1600 hrs. The ambient temperature impact toughness decreases in a non-linear fashion with increasing amounts of σ phase. The impact toughness initially decreases rapidly with precipitation of very small amounts (about 0.01%) of grain boundary σ phase, and then decreases less rapidly with further increases in the amount of the σ phase.

The ambient temperature uniaxial tensile elongation δ and reduction in area ψ also decrease with increasing amounts of σ phase, with the decrease in the elongation being less sensitive to the amount of σ phase than the decrease in the reduction in area. The ultimate and yield strengths do not vary in any significant way with σ phase content.

Fig. 3 shows the effect of long-time exposures up to 1000 hrs at 800°C and up to 10,000 hrs at 700°C and 750°C on ambient temperature impact toughness and tensile elongation in the 15Cr/40Ni type alloy. As with the 15Cr/25Ni type alloys, the impact toughness and the tensile elongation of the 15Cr/40Ni type alloy decrease significantly with increasing exposure times. The μ phase initially precipitates preferentially at grain boundaries, but after long-time exposures (1000 hrs at 800°C, and 10,000 hrs at 700°C and 750°C) the μ phase was seen to precipitate both at grain boundaries and within the grains, see for example Foto. 2. In order to study only the effects of grain boundary μ phase, special heat treatments were chosen for a 15Cr/40Ni type alloy, as already described, that limited the precipitation of μ phase to grain boundaries. Fig. 4 shows the effect of grain boundary μ phase on ambient temperature impact toughness and tensile properties. Small amounts of μ phase (less than ~1%) caused embrittlement, as evidenced by decreased impact toughness, tensile elongation and reduction in area. The ultimate tensile strength was apparently not affected by μ phase formation.

Other properties, such as the high temperature tensile and impact and stress rupture properties were not very sensitive to either precipitation of small amounts of σ phase in the 15Cr/25Ni type alloys or precipitation of small amounts of μ phase in 15Cr/40Ni type alloys.

Fig. 1. The influence of long-time exposure at 650°C on the amount of c phase and ambient temperature impact toughness in 15Cr/25Ni type alloy

Fig. 2. The influence of the amount of c phase on tensile properties and impact toughness at ambient temperature

Fig. 3. The effect of long-time exposures at 700°C-800°C on ambient temperature impact toughness and tensile elongation in 15Cr/40Ni type alloy

Fig. 4. The effect of grain boundary v phase on ambient temperature impact toughness and tensile properties

Fig. 5. The relationship between the ambient temperature impact toughness and the amount of grain boundary v phase in 15Cr/40Ni type alloy

Fig. 6. The relationships between the ambient temperature impact toughness and the amount of grain boundary c phase and the average diameter of dimples on fracture surface in 15Cr/25Ni type alloys. n_1 and n_2 represent different size of grains

The relationships between the ambient temperature impact toughness and the amount of grain boundary μ and σ phases are shown in Figs. 5 and 6, respectively. In these figures, the impact toughness A_K is plotted as a function of the concentration coefficient of grain boundary embrittling phase, η . The concentration coefficient η is defined as $\Sigma l / \Sigma L$, where Σl is the total length of grain boundary covered by embrittling phase (μ or σ) and ΣL is the total length of grain boundary. As seen in Figs. 5 and 6, a linear relation exists between A_K and η , given by

$$A_K = -A\eta + B = -A(\Sigma l / \Sigma L) + B$$

A is a material constant that depends on the type of embrittling phase (σ or μ) and also on the grain size of the alloy. B is also a material dependent parameter that has the value of the impact toughness of the alloy when no embrittling phase is present.

The embrittling effect of σ and μ phases can be controlled in two ways. One way is to control the chemical composition by the PHACOMP method (12), and thereby control the amount of σ phase present. Fig. 7 shows for 15Cr/25Ni type alloys the relationships between both the decrease of impact toughness $-\Delta A_K$ and the amount of σ phase present and the electron vacancy parameter $\Delta N_V'$ (12). If $\Delta N_V'$ is positive, no σ phase is present and embrittlement is suppressed. As the value of $\Delta N_V'$ becomes negative, σ phase begins to appear at grain boundaries and the impact toughness decreases rapidly. As $\Delta N_V'$ becomes more negative, the amount of grain boundary σ phase increases and the impact toughness continues to decrease, but it is seen that the decrease of impact toughness is not proportional to the increase in σ phase.

A second way to influence the embrittling effect of grain boundary σ phase is to control the grain size. Fig. 8 shows the effect of grain size on the relationship between impact toughness and amount of grain boundary σ phase present. Clearly, a decrease in the grain size, keeping the amount of σ phase constant, results in less severe embrittlement. This result implies that processing to achieve an ultrafine grain size will further suppress the embrittlement caused by the grain boundary σ phase.

Fracture Mechanisms

The fracture surfaces of impact specimens of the 15Cr/40Ni type alloys which represent different values of ambient temperature impact toughness are shown in Foto. 3. The specimen without grain boundary μ particles (Foto. 3a) has a relatively high value of impact toughness and the fracture is intragranular. As the μ phase is precipitated at grain boundaries, the mode of fracture during ambient temperature impact testing changes from transgranular fracture to intergranular fracture. The specimen containing a great amount of grain boundary μ phase (Foto. 3c) has a low value of impact toughness and the fracture is completely intergranular. The same trend was found for 15Cr/25Ni type specimens with increasing amounts of grain boundary σ phase.

During tensile testing fracture surfaces exhibiting both intragranular and intergranular features were observed for the 15Cr/40Ni type alloys containing grain boundary μ phase, but only transgranular fracture surfaces were observed for the 15Cr/25Ni type alloys containing grain boundary σ phase, even for very high loading rates up to 20,000 mm/min. Larger decreases in the ambient temperature tensile elongation were observed in the specimens containing grain boundary μ particles than in the specimens with grain boundary σ particles.

Thus, the appearance of the fracture surface is dependent not only on the amount of embrittling phase present at grain boundaries, but also on the type of mechanical test.

A typical fracture surface from an ambient temperature impact test of material with grain boundary σ precipitates is characterized by intergranular dimple formation, Foto. 4. The equiaxed FeCr type σ phase particles, which average about 1 μ m in diameter can be seen in the higher magnification SEM shown in Foto. 5. During impact testing, microcracks are formed at the interfaces between σ particles and the matrix, due to the large differences between the elastic and plastic properties of the brittle σ phase and the ductile γ matrix. Neighboring microcracks link together resulting in intergranular dimple fracture. The average dimple diameter was found to be inversely proportional to the concentration coefficient of grain boundary σ phase, see again Fig. 6. When the concentration of grain boundary σ phase is low, microcracks are formed not only at grain boundary σ particles, but also at other interfaces within grains, such as interfaces between MC carbides and the matrix and between other non-metallic compounds and the matrix. This results in the appearance of

mixed modes of fracture.

The fracture mechanism in 15Cr/40Ni type alloys with grain boundary μ phase appears to be different from the fracture mechanism in 15Cr/25Ni type alloys with grain boundary σ phase. Foto. 6 shows a typical low ductile intergranular fracture surface in an alloy with grain boundary μ phase. This fracture surface is relatively flat, but it is not a cleavage fracture. Under higher magnification, see Foto. 7, the fracture surface has a "porous" or "toad-skin-like" appearance. The grain boundary μ particles which are determined to be about $0.5\ \mu\text{m}$ in diameter in the optical microscope are not observed at the fracture surface, see Fotos. 6 and 7. It seems that only a small part of each μ particle is exposed at the fracture surface. In order to determine if cracking occurs along the interfaces between μ particles and the matrix, an ion-probe analysis was done to determine the change in Mo content (Mo is the major chemical constituent of the μ phase) with depth under the fracture surface. The relative Mo content was measured by the intensity of MoO ion current and the depth under the fracture surface was calculated by sputtering rate of the ion beam. The result of this probe, shown in Fig. 9, indicates that the Mo content in the surface layer is relatively low and changes with the depth under the fracture surface. This implies that the μ particles are not exposed on the fracture surface, but are covered by a thin matrix layer of about 300 Å. The diameter of the μ particle indicated by the ion-probe is consistent with the diameter of about $0.5\ \mu\text{m}$ measured using the optical microscope. It is possible that microcracks initiate at grain boundaries nearby interface regions between the μ particles and the matrix and then connect with other cracks formed in the same way at nearby grain boundary μ particles, resulting in an intergranular fracture surface. Here the μ particles are not found at the base of dimples, as was the case for σ particles, but instead dimples are not formed and μ particles protrude slightly from the matrix. These two fracture mechanisms are schematically described in Fig. 10.

The differences between the two fracture mechanisms may be related to the fact that the concentration coefficient is higher for the alloy with the μ phase than for alloy with σ phase, and to the fact that average diameter of the μ particles is smaller than the average diameter of the σ particles. Perhaps also the cohesive strength between the μ phase and the γ matrix is greater than the cohesive strength between the σ phase and the γ matrix. These mechanisms need to be investigated further.

CONCLUSIONS

1. Small amounts of grain boundary μ or σ phases in 15Cr/40Ni type or 15Cr/25Ni type alloys, respectively, even in the range of 0.01-1%, can cause embrittlement, as evidenced by decreased ambient temperature impact toughness.

2. The degree of embrittlement was found to be directly proportional to the concentration coefficient of μ or σ phases at the grain boundaries. The relationship between the ambient temperature impact toughness A_K and the concentration coefficient η is given by $A_K = -A\eta + B$, where A and B are different material constants.

3. This embrittlement effect results in intergranular fracture. The mechanisms of fracture in the alloys with μ phase and in the alloys with σ phase are quite different. In the case of the alloys with σ phase, intergranular dimple fracture is found; but a "toad-skin-like" intergranular fracture results in the case of the alloys with μ phase.

4. The embrittlement effect can be suppressed by reducing the grain size or by decreasing or removing the grain boundary embrittling μ and σ phase by controlling the chemical composition of the alloys.

REFERENCES

1. C.P. Sullivan and M.J. Donachie Jr.: Metals Eng. Quart., 11, no. 1, 1 (1971).
2. R.F. Decker and S. Floreen: Precipitation from Iron-Base Alloys, Eds. G.R. Speich and J.B. Clark, Gordon and Breach, New York, p. 69 (1965).
3. C.T. Sims: Journal of Metals, 18, 1119 (1966).
4. G.P. Sabol and R. Stickler: Physica Status Solidi, 35, no. 1, 11 (1969).
5. C.T. Sims: The Superalloys, Eds. C.T. Sims and W.C. Hagel, John Wiley & Sons, New York, p. 259 (1972).
6. C.P. Sullivan and M.J. Donachie Jr.: Metals Eng. Quart., 7, no. 1, 36 (1967).
7. J.R. Mihalisin et al., Trans-AIME, 242, 2399 (1968).
8. G.S. Chen, C.C. Yao and Z.Y. Zhong: Acta Metallurgica Sinica (China), 14, No. 3, 284 (1978).
9. H.J. Beattie Jr. and W.C. Hagel: Trans. TMS-AIME, 221, 28 (1961).
10. G.N. Maniar et al., Trans. TMS-AIME, 245, 701 (1969).
11. J.R. Wood: Proc. 3rd Int'l Symp on Superalloys, Seven Springs, PA, p. 227 (1976).
12. G. Chen and X. Xie: Acta Metallurgica Sinica (China), 14, No. 4, 440 (1978).

13. "Research Report on 15Cr/40Ni Type Iron-base Superalloy," Shanghai Iron and Steel Research Institute, Beijing University of Iron and Steel Technology, China, 1978.
14. S.D. Shi et al., Symposium on High-Temperature Alloys, Beijing University of Iron and Steel Technology, China, p. 3-1 (1979).

ACKNOWLEDGEMENT

The authors are grateful to the Mechanical Laboratory at the Shanghai Fifth Steel Plant, the Third and Fourth Research Divisions of the Shanghai Iron and Steel Research Institute and the Chemical Analysis Center of Beijing University of Iron and Steel Technology for technical assistance during portions of this research.

Fig. 7. The relationships between both the decrease of impact toughness $-\Delta K$ and the amount of σ phase present, and the electron vacancy parameter ΔN_y ($\Delta N_y = \text{Ni-3Ti-3.5Al-1.7Si-0.9Cr-4.7}$)

Fig. 8. The effect of grain size on the relationship between impact toughness and amount of grain boundary σ phase

Fig. 9. Ion probe analysis showing the change of Mo content with depth under the fracture surface

Fig. 10. Schematic representation of the different fracture mechanisms caused by grain boundary (a) σ phase, and (b) μ phase