STRUCTURE PROPERTY RELATIONSHIPS OF ZERON 100

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ABSTRACT

The mechanical properties of Zeron 100 duplex stainless steel of nominal composition 25 wt% Cr, 7.5 wt% Ni, 3.5 wt% Mo, 0.5 wt% W, 0.5 wt% Cu, 0.25 wt% N have been determined and compared with those of Uranus 50. The alloy phases present were identified by optical and transmission electron microscopy, electron and X-ray diffraction and electron microprobe analysis. In the solution heat treated condition, the microstructure of both alloys consists of Widmanstätten austenite in a ferrite matrix. Several other phases can form, including σ, M_2X, $M_{23}C_6$ and α' following heat treatments in the temperature range 400 to 1000°C.

After short periods of ageing at 475°C, α' formation results in an increase in tensile strength which is accompanied by a decrease in toughness. Sigma-phase formation occurs during ageing in the temperature range 750 to 1000°C. An excellent correlation has been obtained between isothermal transformation data (TTT curves) for sigma-phase generated using metallographic techniques and impact properties. Sigma-phase formation during continuous cooling, as would occur during casting or cooling from heat treatment, is retarded relative to that predicted from the isothermal transformation data.

1. INTRODUCTION

Centrifugal pumps and associated pipework for seawater, oil and geothermal power purposes are frequently used in conditions of high flow rates (up to 100,000 US gal./min.) and high pressures (differential heads of up to 10,000 ft.) in addition to hostile chemical environments. Equipment of this nature, particularly that associated with offshore oil drilling platforms, must be designed to keep weight to a minimum thus reducing the cost of the supporting structure. To satisfy the criteria outlined above, the materials used for the manufacture of such machinery must combine high strength-to-weight ratios with good corrosion resistance. The latter requirement has become increasingly important in recent years due to the necessity of drilling in 'sour' wells containing increasing quantities of H_2S and CO_2.

Work has been undertaken by Mather and Platt Ltd., in co-operation with the University of Manchester / UMIST Department of Metallurgy and Materials Science, to develop a duplex stainless steel (Zeron 100) based on 25 wt% Cr, 7.5 wt% Ni, 3.5 wt% Mo, 0.5 wt% W, 0.5 wt% Cu, 0.25 wt% N to meet the requirements outlined above. In the course of this work, it has been necessary to determine the effect on mechanical properties of variations in alloy content, particularly of Mn, Mo, N, Cu and W via their influence on phase transformations. These transformations involve the formation of σ, α', $M_{23}C_6$, and γ_2 (refs 1-3). In this investigation, the effect of heat treatment on these transformations, and hence on mechanical properties has been studied for Zeron 100 and compared with those obtained by other workers for Uranus 50 (refs. 4 and 5).

2. EXPERIMENTAL

The composition of the alloy used in this investigation is given in table 1 along with that of Uranus 50. The Zeron 100 was supplied in a forged condition which had experienced a reduction ratio of 9:1. Solution heat treatment was carried out at 1150°C in argon before quenching directly into the ageing medium for isothermal heat treatment. Continuous cooling transformation was preceded by solution heat treatment at either 1150 or 1300°C in air. Isothermal ageing heat treatment was carried out in air in fluidized beds for up to 20 hours at temperatures of between 400 and 1000°C, whilst continuous cooling heat treatment was carried out by furnace cooling.

Specimens for optical metallography were prepared by grinding and mechanical polishing followed by electrolytic etching in 10 % KOH at either 2 or 10 volts. Quantitative metallography was carried out using a 'Quantimet' 720 image analyser.

Thin foil specimens for transmission electron microscopy were prepared by electropolishing in a 'Struers' Tenupol jet polisher at between 30 and 40 volts in a solution of 10 % perchloric acid in acetic acid at room temperature. Transmission electron microscopy (TEM) was carried out at 100 keV with a Philips EM 301 or at 120 keV with a Philips EM 400T analytical electron microscope.

Thin foil microprobe analysis of the various alloy phases was performed in the Philips EM 400T electron microscope using an EDAX energy dispersive X-ray detector. Quantification was by the ratio technique (ref.6) using experimental k-factors.

X-ray diffraction was performed to determine the lattice parameters of sigma-phase on a specimen solution heat treated and subsequently aged at 800°C for 100 hours using a Philips PW 1380 horizontal diffractometer.

Room temperature tensile testing was carried out on the isothermally heat treated specimens using an 'Instron' TTD screw driven tensile testing machine at a cross-head speed of 0.5 mm./min. Charpy impact testing was carried out at -10°C on similarly heat treated v-notch specimens.

3. RESULTS AND DISCUSSION

An example of the microstructure of forged Zeron 100 is shown in fig.1. Typically, the alloy contains 35-45 % ferrite compared with 30-50 % ferrite for Uranus 50 (ref.7), although these figures would depend on the exact chemical composition.

3.1 475°C Embrittlement

3.1.1 Microscopical Observations

Fig.2 shows a transmission electron micrograph of Zeron 100, solution heat treated at 1150°C, water quenched, aged at 475°C for 6 hours and water quenched. The structure consists of a matrix of ferrite with plate-like precipitates of alpha-prime. The ferrite can be identified by electron diffraction and thin foil microprobe analysis spectra of the type shown in fig.3(b). Comparison of the relative heights of the Cr and Fe k_α-peaks can be used to distinguish ferrite from austenite, although quantitative data was obtained and is shown in table 2.

3.1.2 Effects of Alpha-prime on Mechanical Properties

The effects of alpha-prime formation on the mechanical properties of Zeron 100 can be seen in figs. 4, 5, 6 and 7. Of the three temperatures chosen to indicate the ageing response, that of 475°C led to the greatest increase in 0.2 % proof stress (fig.4), UTS (fig.5) and the greatest drop in impact energy (of 200 J below the as-forged value in fig.6). This is also born out by the C-curves shown in fig.7, which were constructed so as to contain proof stress values within given ranges. The increase in proof stress associated with 475°C embrittlement is most marked after ageing at this temperature for 20 hours. (The longest time used in this investigation). The increase in proof stress and decrease in impact energy appear to be associated with the early stages of alpha-prime formation.

When impact data for Zeron 100 is compared with that of Uranus 50, (obtained by Solomon and Devine, fig.8, ref.4), it can be seen that an impact energy drop of 50 ft.lbs. (67.8J) occurs after ageing for about 2 hours at 475°C for both alloys. In addition, a similar drop in impact energy after ageing at 400°C occurs after about 10 hours. The 0.2 % proof stress of Uranus 50 after ageing at 475°C for 2 hours shows an increase of 24 ksi. (165 MPa) from 56 to 80 ksi. (386 to 552 MPa), (table 3). When Zeron 100 was similarly aged, this caused a rise in proof stress from an as-forged value of 570 MPa to 728 MPa; an increase of 158 MPa.(table 4). For both alloys, the effects of an equivalent heat treatment give rise to similar increases in proof stress, although that of Zeron 100 was significantly higher in the as-forged condition.This is probably due to the alloy's higher austenite and nitrogen content, leading to higher rates of strain hardening. The effect of nitrogen on the strength of stainless steels is well known (refs. 8, 9 and 10).

To summarize, 475°C embrittlement leads to similar increases in proof stress and decreases in impact strength in both Zeron 100 and Uranus 50; Zeron 100 has higher proof stress values at all tempering temperatures.

3.2 Sigma Phase Formation

3.2.1 Microscopical Observations

The microstructure of forged Zeron 100 aged at 800°C for 12 hours is shown in fig.9(a). The specimen was etched just sufficiently to reveal sigma-phase without also etching the untransformed ferrite. When compared with the as-received structure shown in fig.14 it can be seen that sigma-phase has formed in the ferrite regions, often adjacent to the ferrite / austenite phase boundaries. In the TEM, the dark etching regions between neighbouring austenite laths can be seen to consist of 'light' and 'dark' phases (fig.10). Energy dispersive X-ray microprobe analysis of the 'dark' phase produced a spectrum of the type shown in fig. 3(c). Quantification yielded the chemical composition shown in table 2 which was in close agreement with that of previous workers for sigma-phase (ref.1). X-ray diffractometry yeilded lattice parameter values for the same phase of a=8.842 Å and c=4.566 Å which agree with previously published data for pure FeCr sigma-phase of a=8.8 Å and c=4.57 Å (ref.11). Thin foil microprobe analysis of the lighter components of the 'cellular' structure resulted in data of the type shown in fig.3(a) which gave quantitative data consistent with that of previous workers for austenite (table 2 and ref.2). Electron diffraction further confirmed the identity of the cellular structure as f.c.c. and body centred tetragonal (sigma-phase) with an orientation relationship of

$(111)_\gamma \parallel (001)_\sigma$; $[\bar{1}10]_\gamma \parallel [\bar{1}10]_\sigma$

This orientation relationship (fig.11) is the same as that found by Nenno and co-workers (ref.12) and by Beckitt (ref.11). Fig.12 shows a particle of sigma-phase nucleated on a ferrite / austenite interphase boundary and apparently growing into the ferrite region. Figs. 13 and 14 show 'fingers' of sigma projecting outwards from the austenite into the ferrite phase regions. In fig.15 sigma growth has reached an extent where the cellular structure has formed, as in fig. 10.

Nucleation of sigma-phase occurs on ferrite / austenite boundaries, presumably due to the good crystallographic match of the (001) plane of sigma and the (111) plane of austenite, which results in the 'Nenno' type orientation relationship (ref.12). Preferential growth of sigma-phase into ferrite occurs because the ferrite is Cr-rich, and as these sigma-phase fingers grow, the surrounding ferrite becomes depleted in Cr and Mo leading to the instability of ferrite and nucleation of austenite. This results in the co-precipitation of austenite and sigma to give a cellular structure. This mechanism of sigma-phase formation is in agreement with that proposed by other workers (ref.13). The transformation is similar in many respects to the eutectoid decomposition in plain carbon steels ie.

$$Fe_\gamma \text{ supersaturated with carbon} \longrightarrow Fe_3C + Fe_\alpha$$

$$Fe_\alpha \text{ supersaturated with chromium} \longrightarrow \sigma(FeCr) + Fe_\gamma$$

3.2.2 Isothermal Heat Treatment

Isothermal ageing heat treatments were performed at temperatures between 650 and 1000°C and for times between 0.5 min. and 10 hours; the specimens were examined on the optical microscope to detect sigma-phase formation. In the graph shown in fig.16, the open circles indicate the absence of sigma-phase whereas the dark circles represent heat treatments where the phase was observed.

3.2.3 Continuous Cooling Treatments

Continuous cooling treatments were carried out in which specimens were furnace-cooled from the solution heat treatment temperatures and withdrawn at temperatures between 1000 and 600°C. The metallographic information is summarized in fig. 18 where the formation of sigma-phase under CCT conditions has been superimposed on the 5% sigma C-curve associated with the TTT heat treatment. Samples have been cooled from both 1150 and 1300°C.

The major difference between the CCT and the TTT results is that sigma-phase formation in the CCT is retarded with respect to the TTT. Increasing the solution heat treatment temperature prior to continuous cooling also has the effect of inhibiting the formation of sigma-phase, as can be seen from the curves in fig.18.

The decrease in the rate of sigma-phase formation in the CCT as compared with that observed in the TTT is probably associated with the relative solute supersaturation produced during the two treatments. In the TTT treatment the solute supersaturation characteristic of the ageing temperature is produced almost instantaneously, which leads to a high nucleation rate of sigma-phase. After an extended time at the ageing temperature, a large number of moderately sized regions of sigma-phase will develop as seen in fig.9(a). In the specimens which have been given the CCT treatment , the solute supersaturation gradually increases as the temperature falls. The initial nucleation of sigma-phase may occur at a higher temperature than in the TTT treatment, but the number of sigma-phase nuclei formed will be less. These nuclei will grow, but produce fewer particles than in the TTT sample, as shown in fig.9(b).

The solution heat treatment temperature prior to cooling determines the grain size and phase balance of the alloy. At 1300°C the structure is almost wholly ferritic with only small regions of austenite, compared with approx 50/50 austenite / ferrite at 1150°C. This in turn affects the chromium concentration of the ferrite due to preferential partitioning of chromium. The lower chromium concentration in ferrite following 1300°C solution heat treatment will decrease the rate of growth of the sigma-phase.

In forging operations and the production of large castings where the component remains at an elevated temperature over a period of time, it is more appropriate to use CCT curves rather than TTT curves as a basis for controlling heat treatment to limit the formation of sigma-phase. If CCT data were used, there would be greater freedom for alloy design and heat treatment without incurring the penalties of sigma-phase formation and the attendant fall in toughness.

3.2.4 Effect of Sigma Phase on Mechanical Properties

The room temperature mechanical properties of Zeron 100 after isothermal ageing at 800°C are shown in table 4. From this it can be seen that 0.2 % proof stress and UTS retain the same values indicating no ductility whatsoever. This is also reflected in the elongation and reduction in area figures which were almost invariably immeasurably low. In contrast, the data for Uranus 50 (table 3) shows some ductility even after ageing at 800°C for 6 hours. Yeilding occurs before the UTS is reached and the reduction in area is much higher at 35 %. The proof stress of Zeron 100 after a 6 hour ageing heat treatment is 732 MPa which is considerably higher than the value of 53 ksi. (=365 MPa) quoted for Uranus 50. This is probably due to the superior as-forged proof stress of Zeron 100 of 570 MPa compared with that of 386 MPa for Uranus 50 (ref.4).

The time taken for a 50 ft.lb. (67.8 J) decrease in impact energy after ageing at 900°C is 0.1 hour for Uranus 50 whereas an equivalent ageing heat treatment for Zeron 100 shows no decrease in impact energy below the as-forged value of 292 J. This indicates that sigma-phase forms more readily in Uranus 50 than Zeron 100.

Fig.17 shows the effect of sigma-phase formation on the impact energy of Zeron 100 after isothermal ageing heat treatments. An excellent correlation exists between this and the C-curve shown in fig.16. Since fig. 16 was plotted using values of volume % sigma-phase from metallographic specimens, this suggests that impact energy is critically dependant on the volume fraction of sigma-phase in the microstructure. The fact that impact energy is so dependant on the presence of sigma-phase has been reported previously by many workers (refs.9, 15 and 16) and as a consequence of this, it is particularly useful in following the extent of the phase transformation.

4. CONCLUSIONS

1. 475°C embrittlement causes similar decreases in toughness in Zeron 100 and Uranus 50, although the impact strength of the former is higher initially.

2. Sigma-phase in Zeron 100 forms at temperatures between 750 and 1000°C on ferrite / austenite boundaries and grows into the ferrite, resulting in a sigma / austenite cellular structure.

3. An excellent correlation exists in Zeron 100 between sigma-phase C-curves obtained both by quantitative metallographic and Charpy impact test techniques.

4. The isothermal ageing behaviour of Uranus 50 and Zeron 100 in the range necessary for sigma-phase formation is similar. However the toughness as measured by impact testing, of Zeron 100 after ageing at 900°C is maintained for slightly longer than for Uranus 50.

5. Sigma-phase formation under continuous cooling conditions in Zeron 100 is retarded relative to that predicted from isothermal transformation data and is additionally retarded when the solution heat treatment temperature is raised from 1150 to 1300°C.

5. REFERENCES

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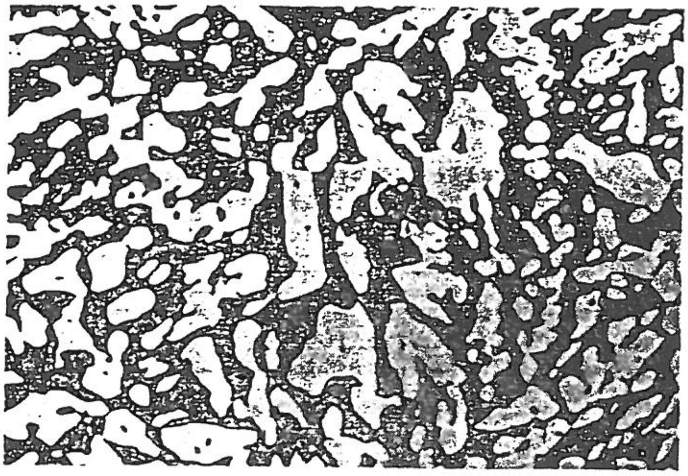
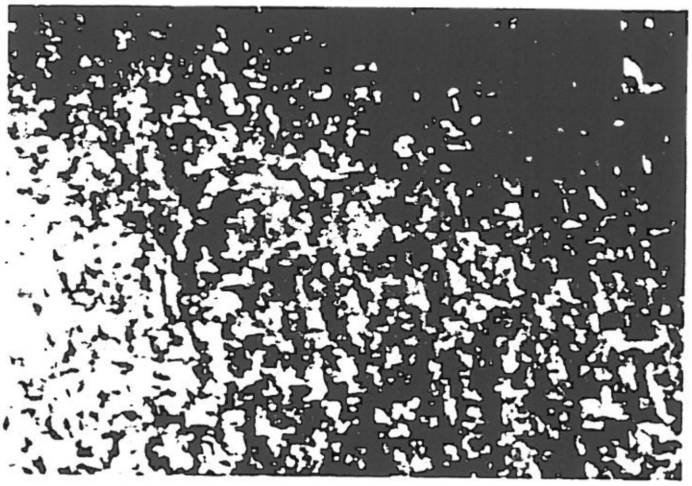
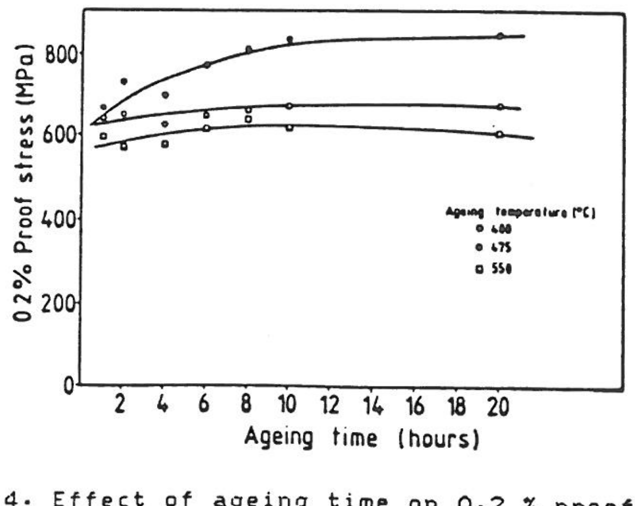


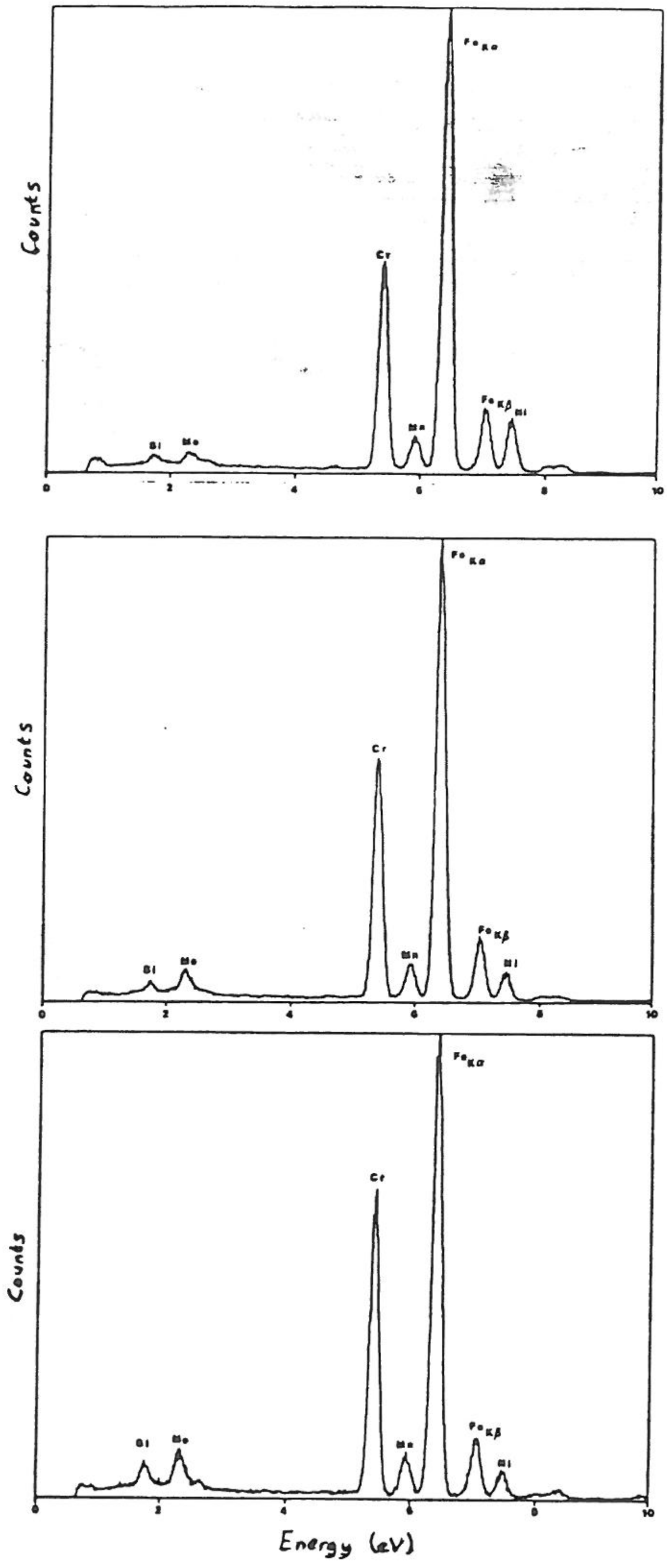
1. Microstructure of forged Zeron 100, solution heat treated at 1150°C



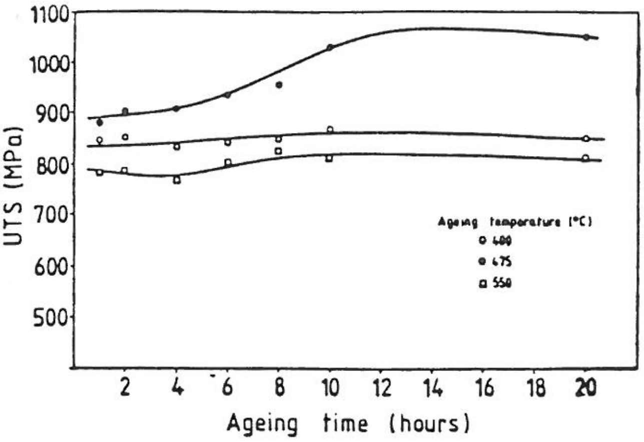
2. TEM micrograph of Zeron 100, solution heat treated at 1150°C for 1 hour, water quenched, aged at 475°C and water quenched (x220000)



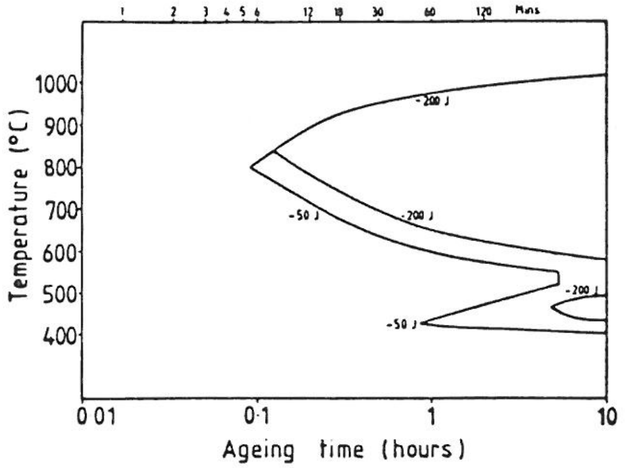
4. Effect of ageing time on 0.2 % proof stress of forged Zeron 100 after solution heat treatment at 1150°C



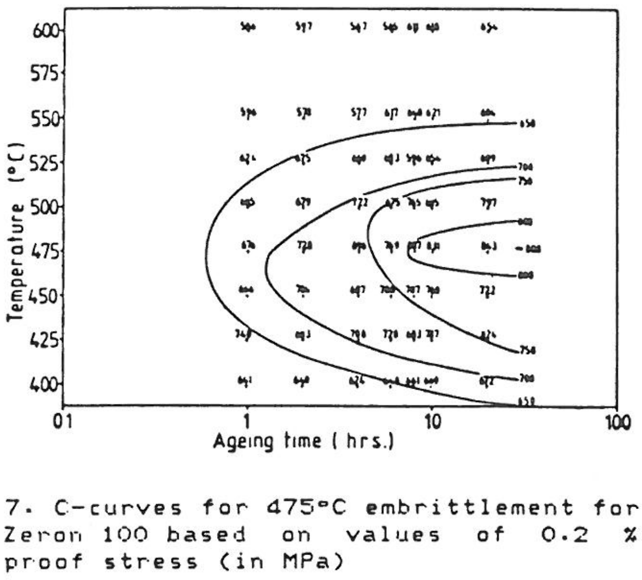
3. Energy dispersive X-ray spectra of (a) austenite, (b) ferrite and (c) sigma-phase in Zeron 100



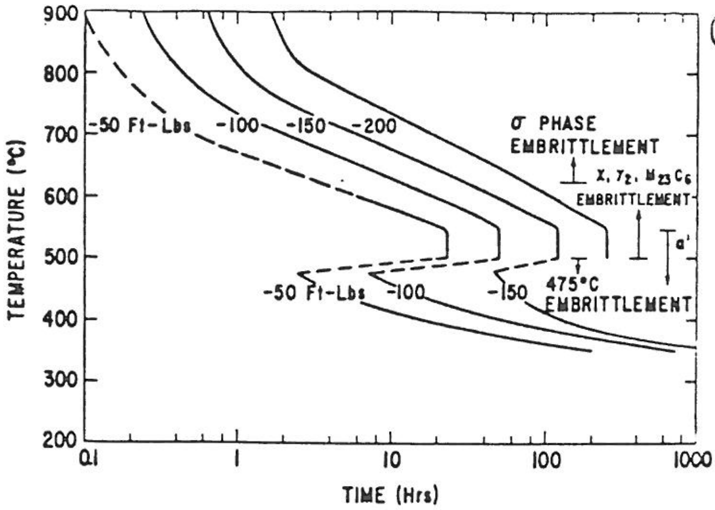
5. Effect of ageing time on UTS of forged Zeron 100 after solution heat treatment at 1150°C



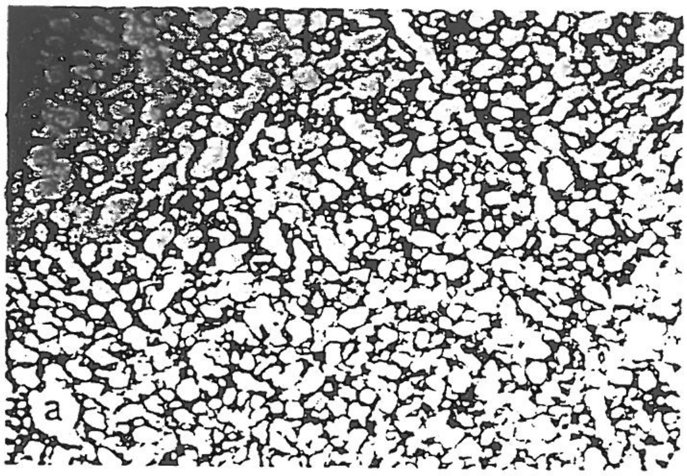
6. Effect of ageing time on decrease in Charpy impact energy (below the as-forged value and at -10°C) for Zeron 100 after solution heat treatment at 1150°C

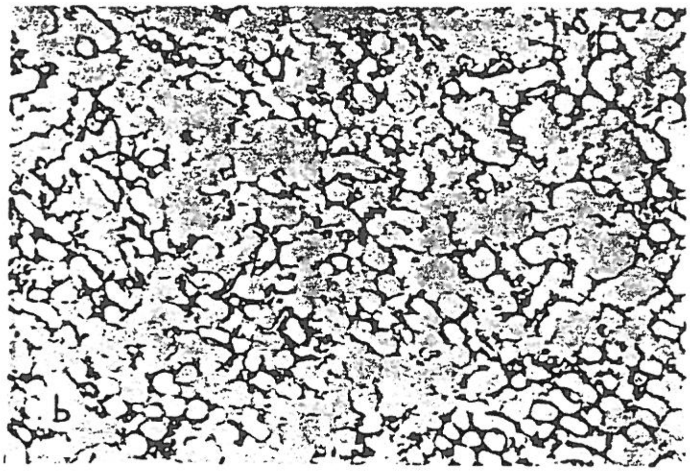


7. C-curves for 475°C embrittlement for Zeron 100 based on values of 0.2 % proof stress (in MPa)

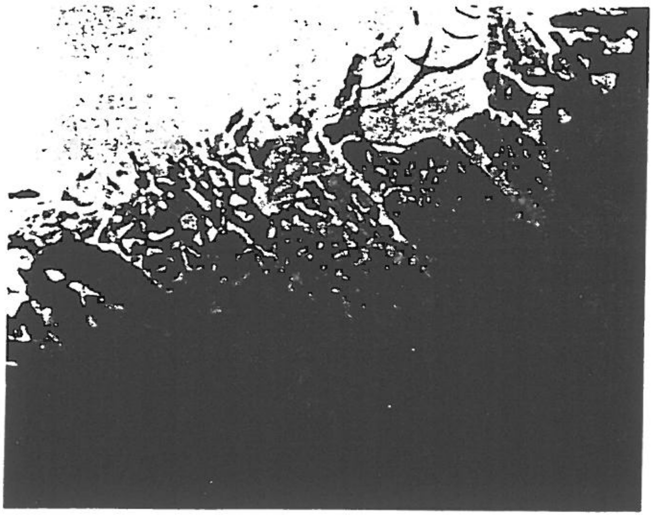


8. Temperature time relationship for a given decrease in Charpy energy for Uranus 50 (refs. 4 and 6) 1ft.lb.=1.356 J)

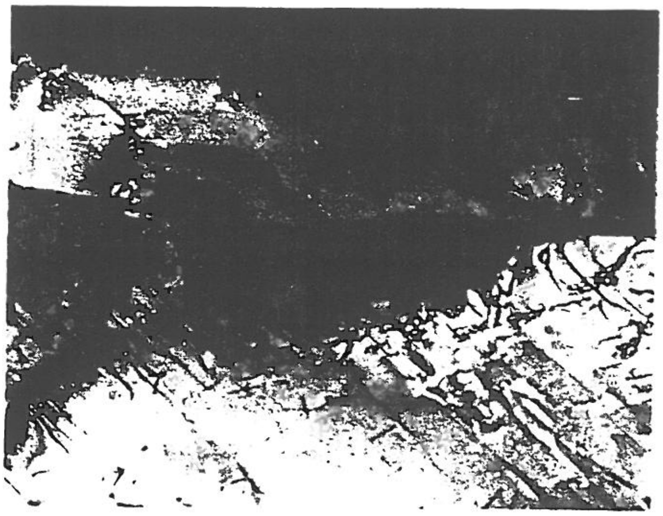




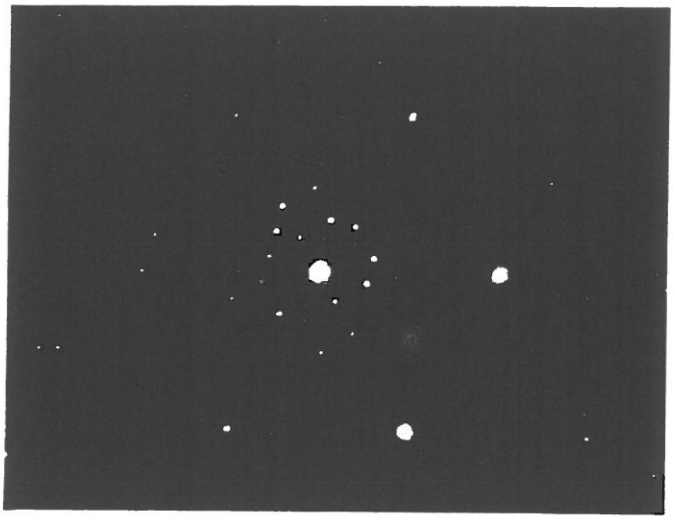
9. Sigma-phase formation in Zeron 100. (a) Solution heat treated at 1150°C for 1 hour, aged at 800°C for 12 min. and water quenched. Sigma-phase has been revealed by lightly etching in 10 % KOH at 2 volts to prevent etching of untransformed ferrite (x400). (b) As above, but slow cooled (CCT) from 1150°C and water quenched from 800°C after 28 min. (x100)



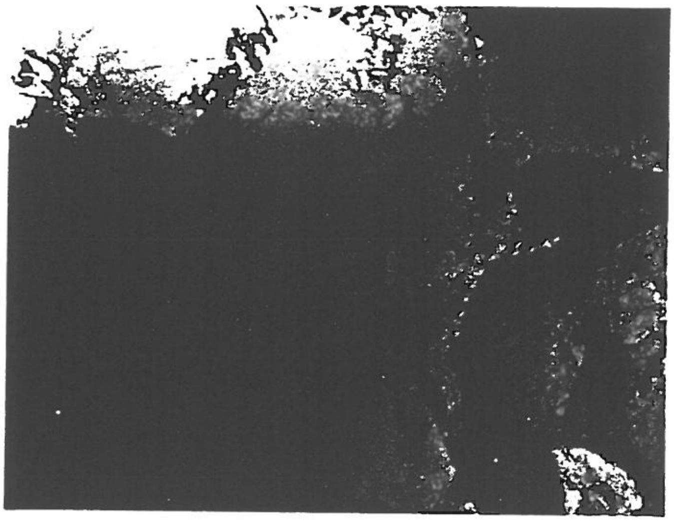
10. TEM micrograph of sigma / austenite cellular structure in forged Zeron 100, aged at 800°C for 18 mins. (x3600)



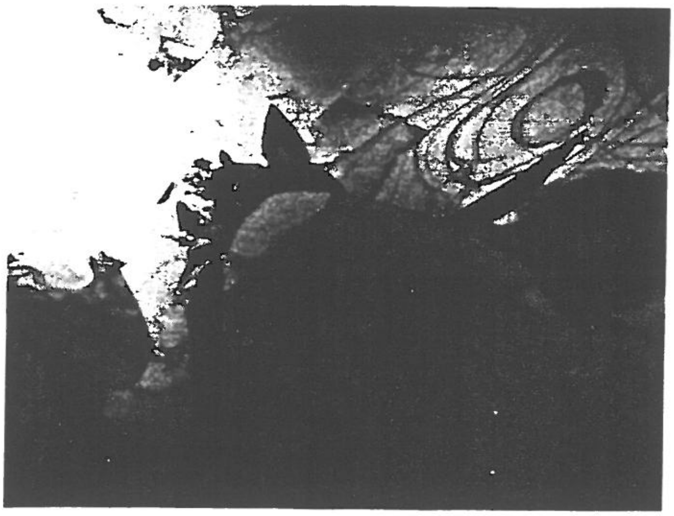
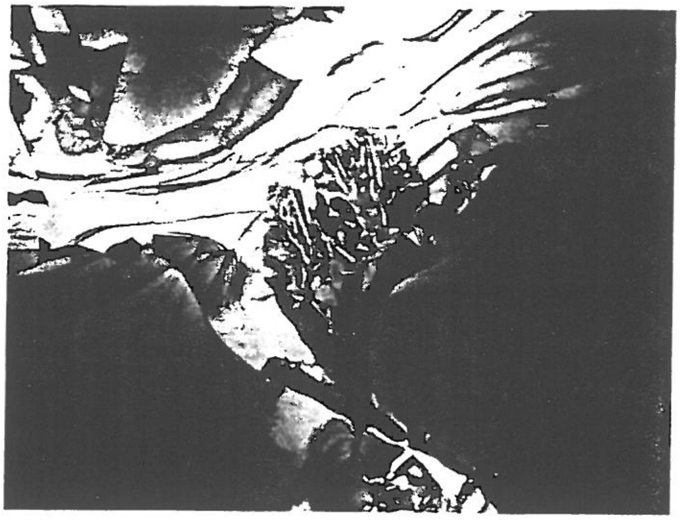
12. Sigma-phase particles on ferrite / austenite boundary growing into ferrite in forged Zeron 100, aged at 800°C for 6 mins. (x28600)



11. SAD pattern showing orientation relationship between (001) and (111) in Zeron 100, aged at 800°C for 100 hours

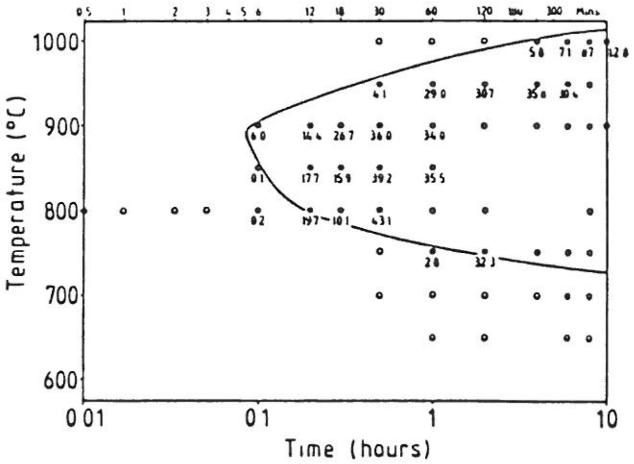


13. Sigma-phase nucleated as in fig.12 and growing into ferrite along ferrite sub boundary, after heat treatment as in fig. 12

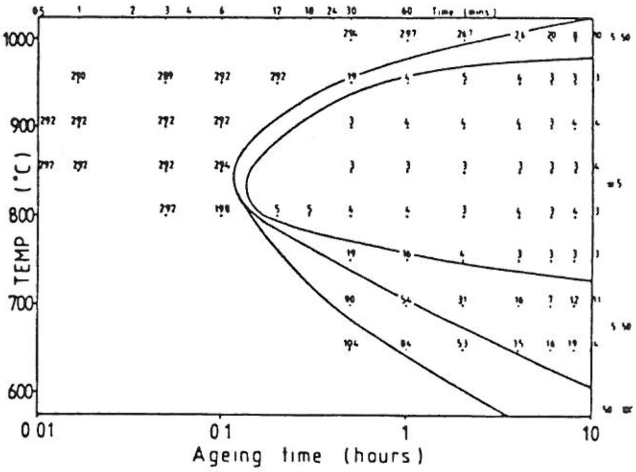
 

14. 'Fingers' of sigma-phase growing into ferrite from ferrite / austenite boundary, in forged Zeron 100, furnace cooled from 1150°C then water quenched after 16 mins. from 900°C (x6800)

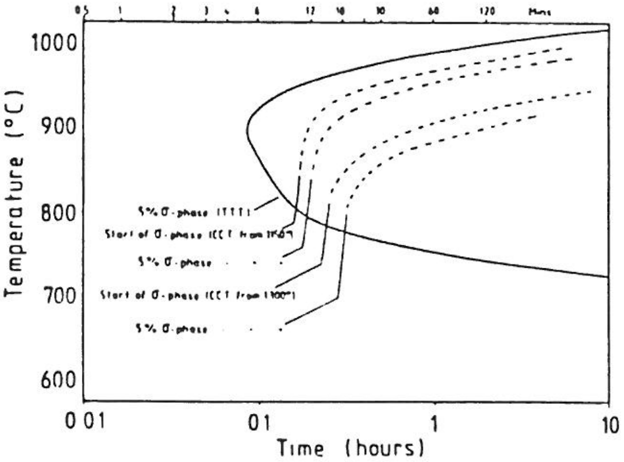
15. Formation of cellular sigma / austenite structure from interphase boundary sigma of the type shown in fig. 13 in material heat treated as in fig. 14 (x4200)



16. C-curve for 5 % sigma-phase formation in forged Zeron 100 based on quantitative metallographic data (vol % sigma-phase)



17. C-curves for sigma-phase formation in forged Zeron 100 based on Charpy impact values (in J)



18. Time temperature transformation (TTT or isothermal) and continuous cooling transformation (CCT) for sigma-phase formation in forged Zeron 100

	Uranus 50*	Zeron 100
Cr	20.0 -22.0	24.0 -26.0
Ni	5.5 - 9.0	6.0 - 8.0
C	0.07 max	0.03 max
N	0.2 max	0.2 - 0.3
Si	na	1.0 max
Mn	na	1.0 max
S	na	0.015 max
P	na	0.025 max
Mo	2.0 - 3.0	3.0 - 4.0
Cu	na	0.5 - 1.0
W	na	0.5 - 1.0

Table 1. Composition of Zeron 100 and Uranus 50 (*ref.6)

0.2% Proof Stress (ksi)	UTS (ksi)	Elong-ation (%)	Area Redn. (%)	Age
80.0	110.5	27	78	475°C/ 2 hr
56.0	87.0	27	80	none
53.0	98.5	17	35	800°C/ 6 hr

Strain rate = 0.1 in/min.
1 ksi = 6.8948 MNm^{-2}

Table 3. Tensile test results for Uranus 50 (ref.4)

	Ferrite	Austenite	Sigma
Si	2.11	2.08	4.50
	0.2	0.2	0.4
Mo	2.06	1.20	2.95
	0.13	0.10	0.21
Cr	29.84	25.52	32.78
	0.57	0.53	0.81
Mn	0.75	1.03	0.5
	0.09	0.11	0.10
Fe	61.16	62.32	55.76
	0.83	0.85	1.08
Ni	4.09	7.85	3.51
	0.23	0.32	0.28

Table 2. Chemical compositions of austenite, ferrite and sigma phases from thin foil microprobe analyses (error figures correspond to 99% confidence limits)

	Ageing Time at 800°C (hours)							
	0.5	1	2	4	6	8	10	20
0.2% proof stress (MPa)	809	828	750	784	732	693	-	731
UTS (MPa)	809	828	750	784	732	693	-	731
%El.	0.1	0	0	0	0	0	-	0
% Area Redn.	0.4	0	0	0	0	0	-	0
Impact Energy (J)	4	4	3	4	3	4	3	3

Table 4. Mechanical properties of wrought Zeron 100 after isothermal ageing at 800°C