JOURNAL OF MATERIALS SCIENCE 17 (1982) 1513–1518

A method for quantitative analysis of delta-ferrite, sigma and $M_{23}C_6$ carbide phases in heat treated Type 316 stainless steel weldments

T. P. S. GILL, J. B. GNANAMOORTHY
Metallurgy Programme, Reactor Research Centre, Kalpakkam 603 102, Tamilnadu, India

Techniques for quantitative estimation of various secodary phases present in austenitic stainless steels were developed using electrochemical and chemical separation procedures. The secondary phases like delta-ferrite, sigma-phase and $M_{23}C_6$ carbide were obtained in pure forms by the electrochemical technique and their anodic polarization behaviours were studied in a sulphuric acid–ammonium thiocyanate medium. The dissolution behaviour of the secondary phases was studied in bromine–methanol solution and the procedures for the separation of delta ferrite-carbide and sigma-carbide mixtures and the quantitative estimation of delta-ferrite, sigma- and $M_{23}C_6$ carbide-phases were standardized.

1. Introduction

When austenitic stainless steel and its weld metal are exposed to elevated temperatures during service, precipitation of various phases such as carbides, chi-phase and sigma-phase takes place. In most of the applications, the chemistry of the welding electrodes is controlled such that a small amount of delta-ferrite [about 3 to 5 ferrite number (FN)] is obtained in the weld in order to avoid hot-cracking and to provide better ductility [1–3]. On exposure to elevated temperatures during service or during post-weld heat treatment, the delta-ferrite constituent in the duplex microstructure tends to transform to intermetallic phases such as sigma-phase and, to a lesser extent, chi-phase. Carbides, particularly the $M_{23}C_6$ type, are also formed especially during the early stages of ageing. Relatively minor amounts of these secondary phases can have major effects on the mechanical and corrosion properties of the stainless steels [1, 4]. Therefore, a knowledge of the type, amount, and physical parameters of all the phases is vital for the achievement of the optimum properties in stainless steels.

Some of the necessary information about the phases present can be obtained from microstructural analysis by physical methods like optical metallography, X-ray diffraction [5], electron microscopy and electron-probe microanalysis. However, for a multi-phase alloy, it is also advantageous to know the precise distribution of elements between the different phases, the quantity of the individual phases and their lattice parameters. This is possible by separating the phases and consolidating them free of matrix contamination. The essential principle of separation of the phases is based on the selective dissolution of the matrix under appropriate conditions. Generally the schemes of separation are based either on chemical or electrochemical techniques. The chemical reagents, like an alcoholic solution of bromine [6], are not always specific. The electrolytic anodic dissolution technique using electrolytes such as hydrochloric acid in a miscible organic solvent [7, 8], is widely used. This electrochemical technique is quantitative for the separation of carbide phases but it is semi-quantitative for the separation of the delta-ferrite and sigma phases [9, 10].

In this paper, a quantitative estimation method comprising of electrochemical and chemical separation procedures is described for estimating secondary phases in aged Type 316 stainless steel weld metals. In the electrochemical method, the

0022–2461/82/051513–06$03.22/0

TABLE I Chemical compositions

Material	Contents (wt%)								
	C	Mn	Si	S	P	Cr	Ni	Mo	Fe
Base metal	0.078	1.10	0.50	0.007	0.009	18.00	10.95	2.00	bal.
Filler wire	0.040	1.26	0.40	0.01	0.013	19.40	12.55	2.28	bal.
Weld metal	0.050	1.23	0.40	0.01	0.012	19.30	12.45	2.25	bal.
Delta-ferrite	–	0.73	0.53	–	–	28.12	5.26	6.15	59.21
$M_{23}C_6$	–	–	–	–	–	61.60	6.10	13.40	18.90
Sigma-phase	–	–	–	–	–	30.20	4.80	8.80	56.20

austenite matrix is selectively dissolved and a binary mixture of phases is obtained. This mixture is then separated chemically.

2. Experimental procedure and results

2.1. Weld metal

A stainless steel Type 316 weld metal was deposited on a Type 316 base plate by the tungsten-inert gas (TIG) process using argon gas shielding. The chemical compositions of the filler wire, weld metal and base metal are given in Table I. The average delta-ferrite content, as measured by Magne-Cage (supplied by the American Instrument Co., Savage, Maryland), was 5.8 FN (ranging from 4 to 8.2 FN).

2.2. Austenite

A specimen from the weld metal (see Section 2.1) was solution annealed at 1373 K for one hour to dissolve the delta-ferrite and subsequently air-cooled to obtain a single-phase austenitic stainless steel.

The anodic polarization curve of the austenitic specimen was obtained in a 3.6 N sulphuric acid–0.1 N ammonium thiocyanate solution. A detailed procedure for obtaining polarization curves has been published elsewhere [11]. The various electrochemical parameters for austenite are given in Table II and the polarization curve is shown in Fig. 1.

2.3. Delta-ferrite

One as-deposited weld metal specimen was treated potentiostatically at −80 mV [relative to the standard calomel electrode (SCE)] in a 3.6 N H_2SO_4–0.1 N NH_4SCN medium to selectively dissolve the austenite phase [11, 12]. After all the austenite was dissolved, a porous mass was left behind. It was chemically cleaned, dried and weighed. The weight of the specimen before dis-

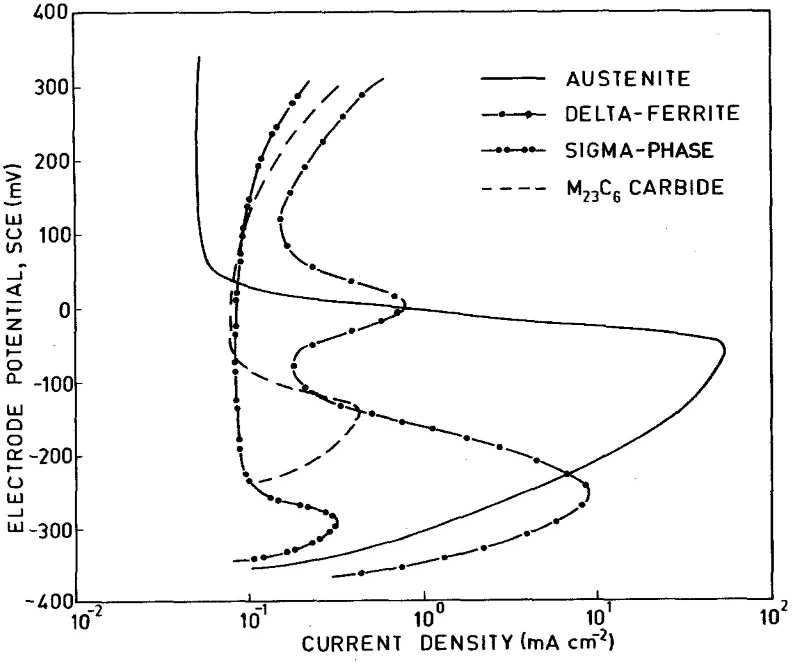

Figure 1 Anodic polarization curves in 3.6 N H_2SO_4 containing 0.1 M NH_4SCN.

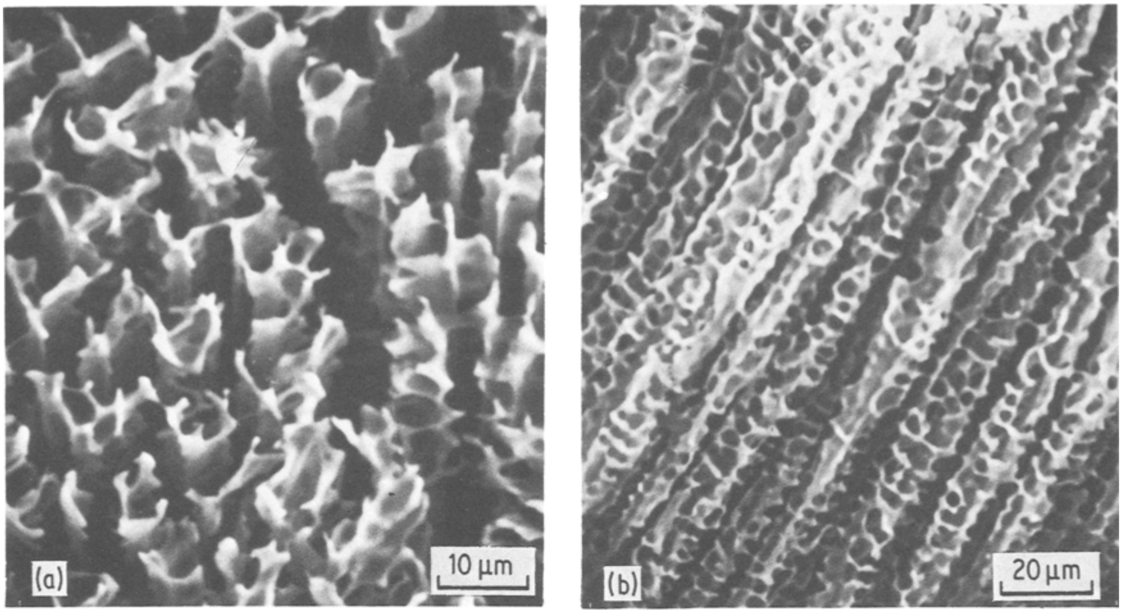

Figure 2 Two photomicrographs of delta-ferrite dendrites taken from two perpendicular cross-sections of a specimen after the austenitic phase was selectively dissolved.

solution and after the completion of dissolution process gave the delta-ferrite content as 3.77 wt%. The two SEM photomicrographs shown in Fig. 2 clearly reveal a three-dimensional network of delta-ferrite. The pores which originally contained austenite were filled with cold-setting epoxy resin. Fig. 3 shows an optical photomicrograph of the polished delta-ferrite specimen. This was used for obtaining the anodic polarization curve for delta-ferrite. The surface area of delta-ferrite was calculated by the "point-count" technique. The chemical composition of delta-ferrite and its electrochemical parameters in a H_2SO_4–NH_4SCN medium are shown in Tables I and II respectively. The anodic polarization curve is shown in Fig. 1.

The dissolution kinetics of pure delta-ferrite was studied in 5% Br_2–CH_3OH solution at room temperature and the results are shown in Fig. 4. The ferrite dissolved completely in about 50 min.

TABLE II Electrochemical parameters of austenite, delta-ferrite, sigma and $M_{23}C_6$ carbide phases in 3.6 N–H_2SO_4 containing 0.1 N–NH_4SCN

Phase	Open circuit potential (mV)	Critical potential (mV)	Critical current density (mA cm^{-2})
Austenite	−380	−55	55
Delta-ferrite	−395	−265	2.5
Sigma	−350	−290	0.33
$M_{23}C_6$	−260	−140	0.47

2.4. $M_{23}C_6$ carbide

Specimens of Type 316 stainless steel base plate were solution annealed at 1373 K for one hour and then aged at 973 K for 20 h, to ensure the precipitation of $M_{23}C_6$ carbide phase. The carbide was

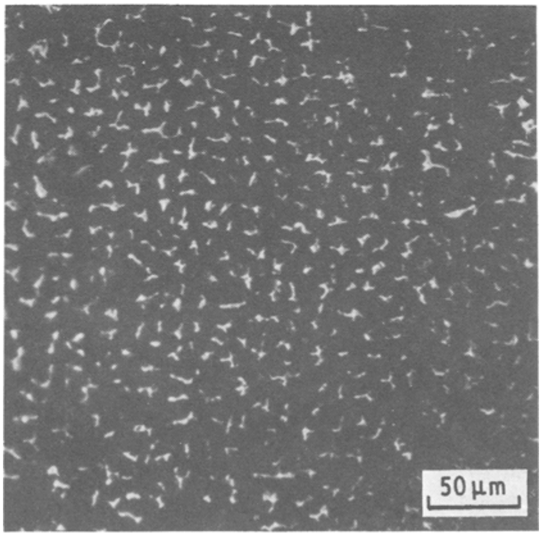

Figure 3 An optical photomicrograph of a delta-ferrite specimen in which the space, where the austenite was present initially, is filled with cold-setting epoxy resin. The photomicrograph corresponds to the side of the specimen shown in Fig. 2a.

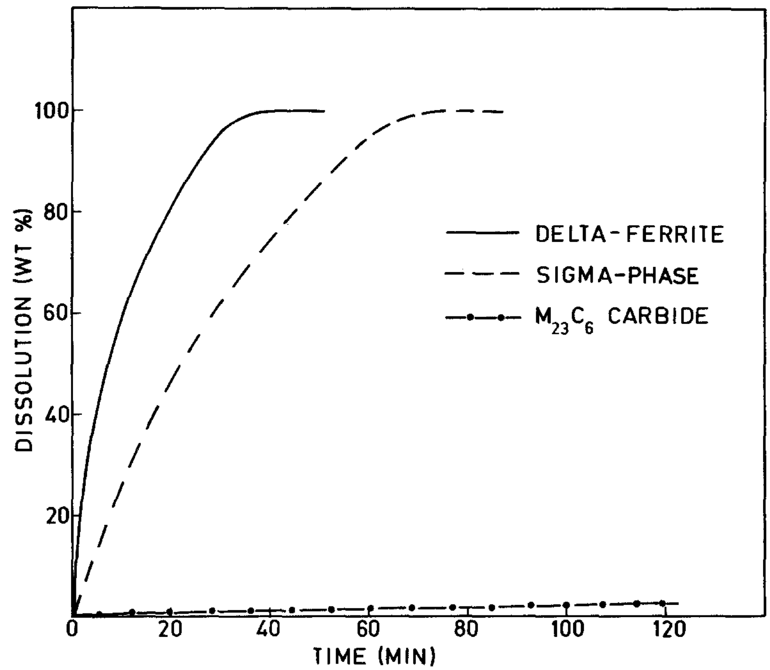

Figure 4 Dissolution behaviour of delta-ferrite, sigma and $M_{23}C_6$ carbide phases in 5% Br_2–CH_3OH solution.

electrolytically extracted in 10% HCl–CH_3OH electrolyte at + 1.5 V potential with respect to a platinum cathode [13, 14]. The residue was collected and analysed by standard X-ray powder diffraction methods. It showed the presence of $M_{23}C_6$ carbide only. A portion of the powder was analysed for its chemical composition and the remaining was compacted into a pellet for obtaining its polarization curve in a H_2SO_4–NH_4SCN medium (Fig. 1). The chemical composition and the electrochemical parameters are reported in Tables I and II, respectively. Fig. 4 shows the dissolution kinetics of pure $M_{23}C_6$ carbide in 5% Br_2–CH_3OH solution. The dissolution rate was comparatively low and only 15.71% of the carbide dissolved in 18 h.

2.5. Sigma-phase

The weld metal specimens containing delta-ferrite were heat-treated at 973 K for 5000 h in quartz capsules evacuated to 10^{-6} Torr pressure. The delta-ferrite under these conditions transforms to sigma-phase and $M_{23}C_6$ carbide [15]. After ageing, the specimens were found to be non-magnetic, thus indicating the absence of delta-ferrite. Fig. 5 shows an optical photomicrograph of one of the aged specimens. The austenite matrix was electrochemically dissolved in a H_2SO_4–NH_4SCN medium at − 80 mV (SCE). The precipitate thus obtained was analysed by X-ray diffraction methods. It indicated the presence of sigma- and $M_{23}C_6$ carbide-phases. The residue was then compacted into a pellet and its anodic polarization curve taken in the dissolving medium. The curve, shown in Fig. 6, was marked by two prominent activity peaks, one at − 290 mV and the other at − 140 mV. The activity peak at − 140 mV was because of the presence of $M_{23}C_6$ carbide (Table II).

To obtain pure sigma phase, the austenite and

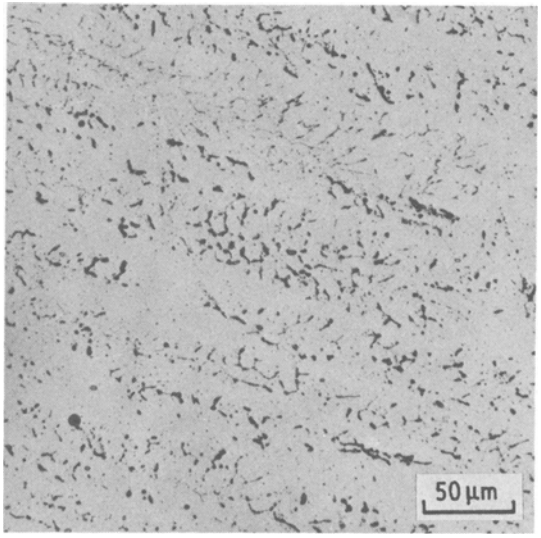

Figure 5 The optical micrograph of a weld metal specimen aged at 973 K for 5000 h. The photograph shows the presence of sigma phase. Etchant: modified Murakami Reagent.

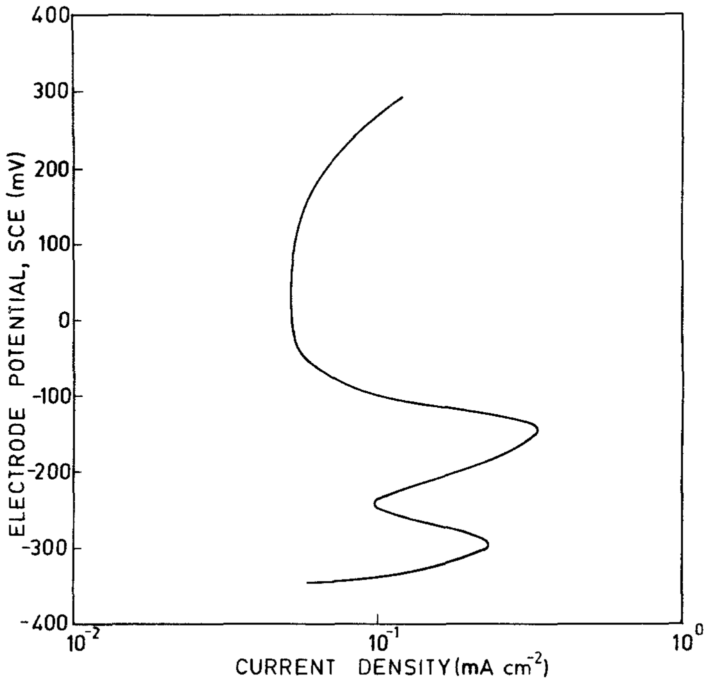

Figure 6 Anodic polarization curve of a mixture of sigma and $M_{23}C_6$ carbide phases in 3.6 N H_2SO_4 containing 0.1 N NH_4SCN.

$M_{23}C_6$ carbide phases of one of the aged specimens were dissolved at − 150 mV (SCE) in the H_2SO_4–NH_4SCN medium. At this potential, both austenite and carbide dissolved and sigma remained in the passive state (Fig. 1). The potential was kept impressed till the current flowing through the system fell to a low value and remained constant, thus indicating the completion of the dissolution process. All the insoluble particles were collected by centrifuging the solution. The X-ray diffraction analysis of the powder showed the presence of sigma-phase only. The precipitate was compacted into a pellet and its anodic polarization curve obtained (Fig. 1). The chemical composition and the electrochemical parameters are reported in Tables I and II respectively. The dissolution kinetics of sigma-phase in 5% Br_2–CH_3OH solution is shown in Fig. 4. The sigma-phase dissolved completely in about 70 min in this medium.

3. Discussion

3.1. Electrolytic separation

For separating secondary phases from austenitic stainless steels, 10% HCl–CH_3OH electrolyte is widely used [10, 13, 15, 16]. In this medium the stainless steel phases like austenite, delta-ferrite, sigma-phase, $M_{23}C_6$ carbide etc., do not show active–passive behaviour. At the potential used for extracting secondary phases from austenite (+ 1.5 V), delta-ferrite and sigma-phase also dissolve at a finite rate, whereas $M_{23}C_6$ carbide does not dissolve actively as it remains in its cathodic range [9]. But in H_2SO_4–NH_4SCN medium, it was found (Fig. 1 and Table II), that between − 55 mV and − 140 mV, only the austenite phase dissolved and the secondary phases remained in their passive states. The relatively high values of the passive currents of various phases indicated by their anodic polarization curves (Fig. 1) obtained by the semi-potentiostatic polarization method were, however, found to be fairly low when the potential was maintained in their passive ranges (truly-potentiostatic condition) as encountered during the extraction process. The fact that the secondary phases exist in their passive states at the dissolution potential (− 80 mV) in the H_2SO_4–NH_4SCN medium as compared to that in the HCl–CH_3OH medium, makes a quantitative separation of these phases from austenite matrix possible. However, the HCl–CH_3OH medium is better than the H_2SO_4–NH_4SCN medium for the estimation of $M_{23}C_6$ carbide since it remains in its cathodic range in the former electrolyte. As a typical example, the estimation by using the alcoholic electrolyte gave 0.49 wt% carbide as compared to 0.44 wt% obtained using aqueous electrolyte, indicating the loss of some carbide by dissolution in the latter medium.

3.2. Chemical separation

While it is possible to individually separate various phases from the austenitic stainless steel matrix by careful adjustment of electrode potentials by a potentiostat, a more convenient technique is to separate the secondary phases from the austenite by an electrochemical method and then individually separate the phases by selective chemical dissolution, since preparation of the powders of the secondary phases into electrodes for electrochemical separation is a very involved and time consuming process. A 5% Br_2–CH_3OH solution was employed to chemically dissolve the delta-ferrite, sigma- and $M_{23}C_6$ carbide-phases, which were obtained by electrochemical extraction method in their pure states. Fig. 4 shows that the delta-ferrite and sigma-phases dissolve rapidly in this solution and dissolution is complete in 50 and 70 min, respectively. But the dissolution rate of $M_{23}C_6$ carbide is relatively low. In 70 min, when the delta-ferrite- and sigma-phases are dissolved completely, only about 1% $M_{23}C_6$ carbide dissolved.

Therefore, a combination of electrochemical and chemical separation methods can be used for accurate weight-fraction determination of secondary phases present in aged austenitic stainless steel. The present method can quantitatively separate austenite–delta-ferrite–$M_{23}C_6$ carbide and austenite–sigma–$M_{23}C_6$ carbide phase combinations and makes the determination of chemical composition of the individual phases possible.

4. Conclusions

The following conclusions can be drawn:

(a) The anodic polarization curves of austenite delta-ferrite, sigma and $M_{23}C_6$ carbide phases of Type 316 stainless steel were obtained in a H_2SO_4–NH_4SCN electrolyte. The curves showed that the austenite phase could be potentiostatically dissolved, at the same time keeping the secondary phases in their passive states.

(b) The chemical dissolution behaviour of secondary phases in Br_2–CH_3OH solution indicated the possibility of quantitative separation of delta-ferrite and sigma-phase from delta-ferrite–carbide and sigma–carbide phase mixtures.

(c) The combination of electrochemical and chemical methods promises a better accuracy.

Acknowledgements

The authors express their gratitude to Dr P. Rodriguez, Head, Metallurgy Programme, for his helpful suggestions and keen interest throughout this investigation. Thanks are also due to Mr Baldev Raj for a critical reading of the manuscript.

References

1. R. G. GUNIA and G. A. RATZ, "The Measurement of Delta-Ferrite in Austenitic Stainless Steels", Welding Research Council Bulletin number 132 (Welding Research Council, New York, 1968).
2. P. RODRIGUEZ, D. K. BHATTACHARYA and S. L. MANNAN, in Proceedings of the Indian Institute of Welding Seminar on Welding of Stainless Steels and Heat Resistant Steels, Bombay, December 1976 (Indian Institute of Welding, Bombay) p. 1.
3. W. T. DELONG, *Welding J.* **53** (1974) 273.
4. C. R. BRINKMAN, V. K. SIKKA and R. T. KING, *Nucl. Tech.* **33** (1977) 76.
5. J. K. L. LAI and I. F. GALBRAITH, *J. Mater. Sci.* **15** (1980) 1297.
6. E. M. MAHALA and N. A. NIELSEN, *Trans. ASM* **43** (1951) 290.
7. W. KOCH, *Stahl Eisen* **69** (1949) 1.
8. T. P. HOAR and K. W. J. BOWEN, *Trans. ASM* **45** (1953) 443.
9. W. SCHUFFENHAUER, *Microchim. Acta* Suppl. 7 (1977) 487.
10. J. M. LEITNAKER, R. L. KLUEH and W. R. LAING, *Met. Trans.* **6A** (1975) 1949.
11. T. P. S. GILL, R. K. DAYAL and J. B. GNANAMOORTHY, *Welding J.* **58** (1979) 375.
12. A. BATHILY, Ph.D. Thesis, University of Paris, France (1974).
13. J. M. LEITNAKER, G. A. POTTER, R. H. SHANNON, D. P. EDMONDS, R. S. COURSE, K. F. RUSSELL and C. W. HOUCK, ORNL-5400 (Oak Ridge National Laboratory, 1978).
14. J. M. LEITNAKER and J. BENTLEY, *Met. Trans.* **8A** (1977) 1605.
15. F. R. BECKITT, *J. Iron Steel Inst.* **207** (1969) 632.
16. B. WEISS and R. STICKLER, *Met. Trans.* **3** (1972) 851.

Received 9 July
and accepted 19 October 1981