JOURNAL OF MATERIALS SCIENCE 16 (1981) 1975–1979

Time dependence at 600 and 650 °C of $M_{23}C_6$ precipitate composition in AISI 304 stainless steel

A. BOEUF. R. COPPOLA, F. ZAMBONADI
Commission of the European Communities, J.R.C., Ispra Establishment, Italy and Institut Laue-Langevin, Grenoble, France

J. P. MORLEVAT
Département de Métallurgie, C.E.N. Grenoble, France

F. RUSTICHELLI
Facoltà di Ingegneria, Università, Ancona, Italy

D. WENGER
Centro Informazioni Studi Esperienze, Segrate, Milani, Italy

The composition of $M_{23}C_6$ precipitates in thermally treated AISI 304 stainless steel was investigated as a function of ageing time at $T = 600$ and 650° C using X-ray fluorescence induced by electron bombardment. With increasing ageing time, it appears that the $M_{23}C_6$ precipitates become progressively enriched in Cr and depleted in Fe. However, a tendency towards saturation appears, the Cr content being higher at $T = 650°$ C.

1. Introduction

Knowledge of the chemical composition of carbide precipitates in austenitic stainless steels is traditionally interesting in order to facilitate a better understanding of the corrosion mechanism. In fact it seems that chromium depletion associated with the precipitation phenomenon is one of the major reasons for the beginning of the corrosion process.

After Goldschmidt's general investigation [1] of the structure of carbides in alloy steels, Philibert *et al.* [2] determined the chemical composition of $M_{23}C_6$ precipitates in Ni–Cr austenitic steels and Da Casa *et al.* [3] determined the composition of $M_{23}C_6$ in 18-8 high-purity and commercial stainless steels. Danyluk *et al.* [4] used Auger electron spectroscopy to investigate the stoichiometry of $M_{23}C_6$ precipitates in 304 stainless steel previously submitted to creep deformation conditions (5.5 MPa at 700° C for 4 Msec in an argon environment) corresponding to the secondary stage. They conclude that the carbides formed at the grain boundaries are of the type $(Fe, Cr)_{23}C_6$, containing mainly chromium with some iron incorporated into the lattice.

Here we report the results of measurements, concerning the content of different metallic elements (M), by assuming that the stoichiometry is $M_{23}C_6$. The composition was investigated as a function of ageing time at $T = 600$ and 650° C using the X-ray fluorescence induced by electron bombardment.

In addition to the traditional and intrinsic interest, our work is particularly interesting as it concerns neutron small-angle scattering investigation of aged and crept samples of AISI 304. This research is related to the study of damage in austenitic stainless steels suitable for use in nuclear fission and fusion reactor technology (Reactor Safety Program and Fusion Reactor Technology Program of the Joint Research Centre of the Commission of European Communities).

Neutron small-angle scattering can provide the total surface and total volume of the precipitates normalized to the unit volume of the sample, if the coherent scattering cross-section curves are

0022–2461/81/071975–05\$02.50/0

known, for each sample [5, 6]. However, in order to evaluate the coherent scattering cross-sections, for a given sample, the difference in the coherent scattering length density of the matrix and that of the precipitates must be known. As such a density depends on the chemical composition of the precipitates, the need for determination of the chemical composition of the carbides in each sample is obvious.

2. Experimental Procedure

The samples were disc-shaped, 1 mm thick and 25 mm diameter. The chemical composition of the AISI 304 used is:

Element	Cr	Ni	Mn	C	Mo	S	P	Si	Fe
wt %	18.12	10.56	1.37	0.069	0.37	0.014	0.027	0.34	bal.

All the samples were submitted to solution treatment at 1050° C for 30 min and then water-quenched. Subsequently, ageing was performed at $T = 600$ and 650° C for 26 to 2330 h. The samples were electrolytically polished to a thickness of 100 μm, then 3 mm diameter discs were obtained and carbon-coated on both sides by evaporation under vacuum. After matrix dissolution in an alcoholic 10% bromine solution, only the carbide precipitates remained between the two carbon films. Standard electron microscopy Al grids were used to remove the samples from the solution and to wash them in CH_3COCH_3 and ethanol. The use of Al ensures that no fluorescence phenomenon is induced in the analysed elements by X-ray radiation.

Analytical determinations were performed using a CAMECA MEB 07 scanning electronic microscope (SEM) equipped with the TRACOR NS 880 system, which analyses the energy spectrum of X-rays emitted by the sample. Measurements were performed at 20 kV for 100 and 800 sec depending on the signal intensity.

As the irradiated portion of the sample was unknown, only the concentration ratios of the different elements could be determined. It was assumed that the samples were very thin so that the correction factors allowing the determination of composition ratios from the intensity ratios are composition independent [7]. This assumption is supported by the fact that the thickness of the carbides is unknown, but is generally less than a few hundred Ångstroms. The ZAF procedure as described in [7] would lead, in this case, to a correction of a few percent, which is much less than other uncertainties.

3. Results and discussion

Before preparation of the samples for composition analysis, a systematic investigation of the carbide precipitation phenomenon was performed at the Ancona University by transmission electron microscopy (TEM). A typical picture for a sample aged at 600° C for 528 h is shown in Fig. 1, in which two kinds of precipitates grow up in epitaxy with the crystallographic fcc lattice axes of the matrix. The first ones are preferentially triangular platelets whereas the second ones are polyhedral particles. Fig. 2 shows the sample aged at 600° C for 2328 h. Both types of precipitates are visible. The density of the precipitates is, in this case, much higher than in the previous picture.

Fig. 3 shows the sample aged at 650° C for 528 h. The intragranular precipitates are easily visible, whereas the intergranular ones are more difficult to see. A sample aged at 650° C for $t = 1992$ h is shown in Fig. 4. A high-density of intragranular precipitates are seen, whereas only a few intergranular ones are visible.

From other observations one can conclude that,

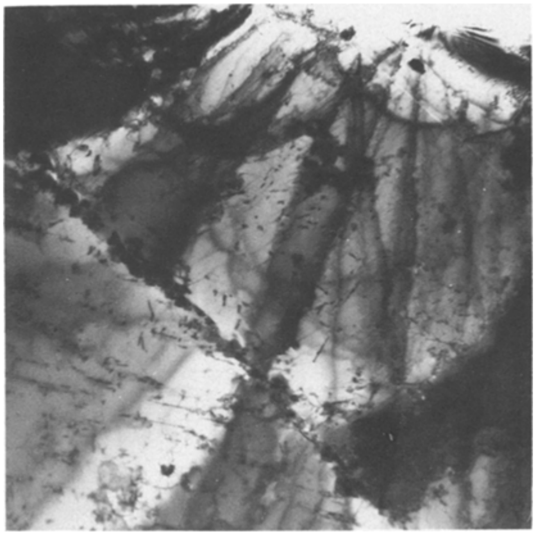

Figure 1 Transmission electron micrograph of AISI 304 stainless steel aged sample ($T = 600°$ C, $t = 528$ h). Both intergranular and intragranular $M_{23}C_6$ precipitates are visible, × 12 831.

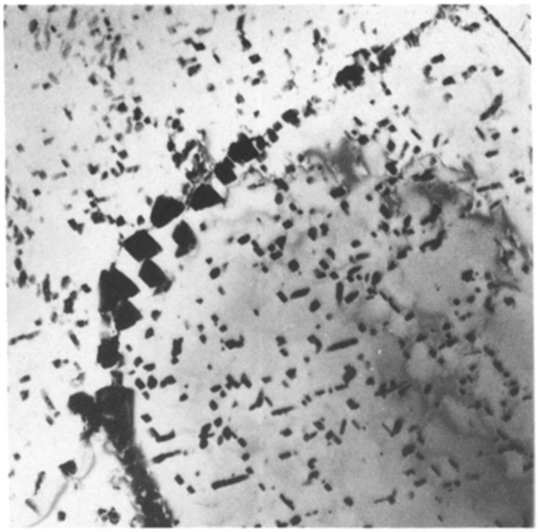

Figure 2 Transmission electron micrograph of AISI 304 stainless steel aged sample ($T = 600°$ C, $t = 2328$ h). × 21 150.

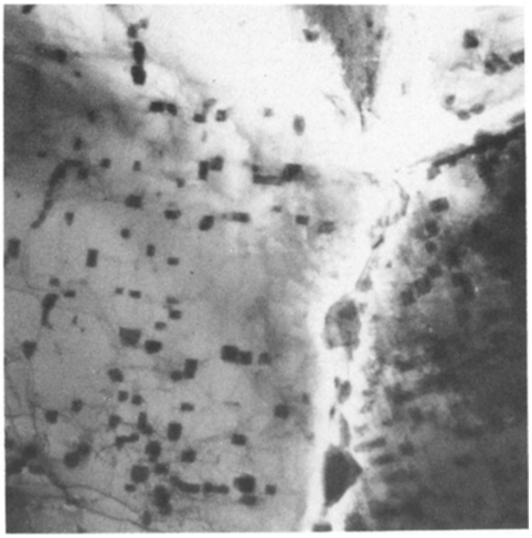

Figure 4 Transmission electron micrograph of AISI 304 stainless steel aged sample ($T = 650°$ C, $t = 1992$ h). × 15 510.

in general, grain-boundary precipitates are formed for ageing times less than those corresponding to intergranular precipitate formation. The trend observed in Figs 1 to 4 of an increase in the density of precipitates with increase in ageing time, is confirmed by other observations.

The linear dimensions of the intergranular precipitates do not appear to change very much from one temperature to another and they range from ~ 500 to 2500 Å. The intergranular precipitates are smaller than the previous ones and their linear dimensions range from ~ 300 to ~ 800 Å at both temperatures.

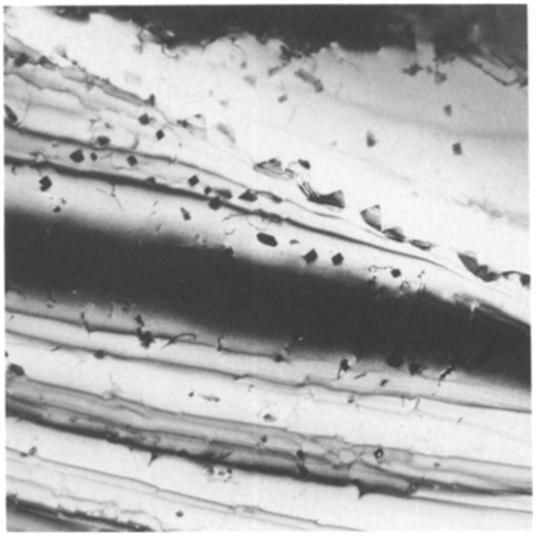

Figure 3 Transmission electron micrograph of AISI 304 stainless steel aged sample ($T = 650°$ C, $t = 528$ h). × 15 510.

Fig. 5 shows a transmission electron micrograph of a sample after carbide extraction treatment recorded before microanalysis. The two families of carbides can be easily identified. The intragranular one appears to be darker than the other. This is due to their thickness. The grain boundary carbides appear as triangular platelets having a common spatial orientation. This common orientation was confirmed by electron diffraction: Fig. 6 shows the diffraction pattern obtained by irradiating a region containing only triangular platelets. In fact the pattern obtained is quite similar to that of a single crystal. This also confirms the epitaxial growth of these carbides.

On the other hand, Fig. 7 shows the electron diffraction pattern obtained by irradiating a region containing mainly intragranular precipitates. Debye–Scherrer rings are now visible, indicating that this kind of precipitate is randomly oriented. However, it is quite possible that this random orientation is consequent to the matrix dissolution treatment and to the polyhedral shape of these carbides and that a certain orientation order also exists in the matrix in this case.

Attempts were made to demonstrate differences in the composition of the two families of precipitates. No difference was detected within the limits of SEM resolution. Therefore the data, which will

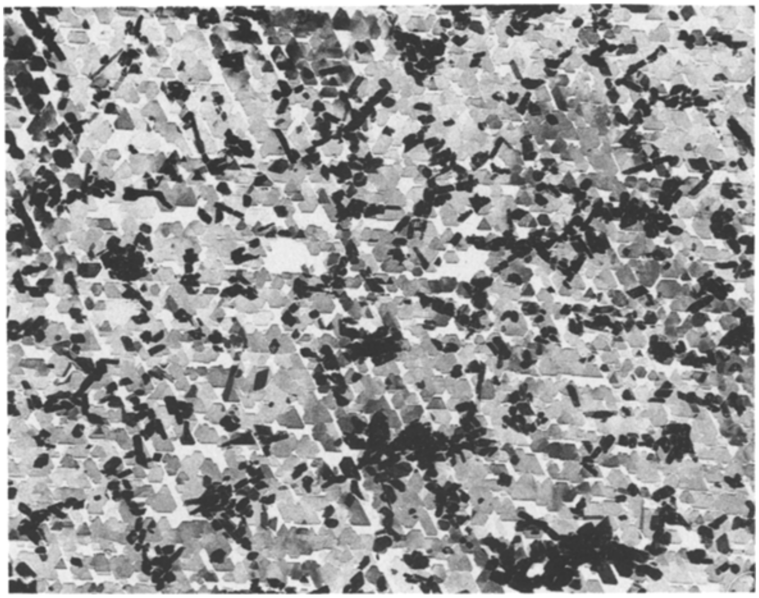

Figure 5 Transmission electron micrograph of an extraction replica from an AISI 304 aged sample ($T = 600°$ C $t = 1656$ h).

be presented, refer to an average value over all the carbides in each sample. In fact, each experimental point was obtained by averaging five different values of composition ratio inside the same sample.

The differences between the data associated with the different regions of a sample are of the same order of magnitude of the statistical uncertainties associated with the X-ray counting. The obtained X-ray spectra show that the carbides investigated contain mainly Cr and Fe and other elements like Mo or Ni only in negligible quantities. Therefore, the weight ratio of Cr/Fe only was plotted in Fig. 8 as a function of ageing time at 600 and 650° C. It appears that initially for both temperatures, increasing the ageing time

Figure 6 Electron diffraction pattern of a region of the sample shown in Fig. 2 containing only intergranular precipitates (triangular platelets).

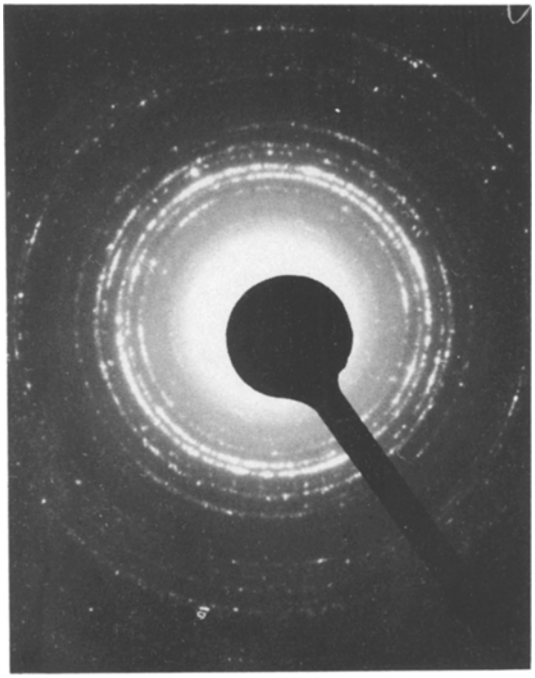

Figure 7 Electron diffraction pattern of a region of the sample shown in Fig. 2 containing mainly intragranular precipitates (polyhedral particles).

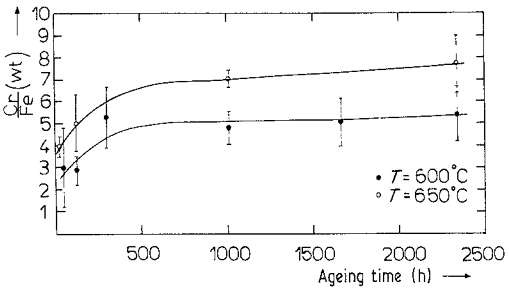

Figure 8 The weight ratio Cr/Fe as a function of ageing time in $M_{23}C_6$ precipitates in AISI 304 stainless steel at $T = 600$ and 650° C.

causes the carbides to become progressively enriched in Cr, in agreement with previous results. Furthermore a tendency towards saturation appears in both cases, the Cr content being higher at $T = 650°$ C.

A similar tendency towards different final values was observed [3] in the 18-8 commercial stainless steel. Probably, as stated in [3], this is a consequence of the temperature dependence of the equilibrium substitution of iron in the $Cr_{23}C_6$ lattice. Also in the case of the 18-8 commercial stainless steel, the final values of the Cr/Fe ratios were higher for higher temperatures. On the other hand, the absolute values of the Cr/Fe ratios obtained in the present experiments appear to be generally higher compared to the values obtained previously for other steels and reported in [3], taking into account the different ageing temperatures. This behaviour can be attributed to the composition difference between the AISI 304 stainless steel investigated in the present work and the stainless steels previously investigated and different solution treatments.

Acknowledgements

It is a pleasure to thank Professor G. Piatti and G. Robert for useful discussions, Dr Matera for performing the ageing treatments, Mr A. Benvenuti, Mr V. Carbone, Mr M. Chaudet, Mr J. Dessus and Mr G. Nombalais, for valuable technical assistance.

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Received 15 October 1980 and accepted 12 January 1981.