Composition of MC precipitates in a titanium stabilized austenitic stainless steel

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A titanium stabilized 18-12 type stainless steel was statically aged at 700 and 750° C, and the resulting MC precipitates were analysed using atom-probe field-ion microscopy. For all ageing times studied (from 3 to 1170 h), the MC particles were found to contain chromium in addition to titanium and carbon. The chromium content was found to decrease from 14 to 5 at% during ageing at 700° C, whereas the carbon content increased from 40 to 50 at%. The effects of precipitate composition on the particle–matrix interfacial energy and on the stability of MC relative to $M_{23}C_6$ are discussed.

1. Introduction

Austenitic stainless steels intended for high temperature service are often given additions of strong carbide-forming elements. The purpose of these additions are two-fold: firstly, to stabilize the microstructure against the formation of $M_{23}C_6$ grain boundary carbide, thereby preventing intergranular stress corrosion; and secondly to obtain a fine dispersion of MC-type carbides which provides an increased creep resistance.

In a recent study using electron microscopy, Thorwaldsson and Dunlop [1] compared the particle growth rates in several stabilized 18-12 type austenitic stainless steels during static ageing at 750° C. They found that in certain alloys after long ageing times, MC precipitates were not stable against the formation of matrix $M_{23}C_6$. A similar observation of a transformation of TiC to $M_{23}C_6$ in a 20Cr–30Ni alloy at 800° C has been made by Howell, Nilsson and Dunlop [2].

In view of this observed transformation to $M_{23}C_6$, it seemed interesting to study the composition of MC precipitates in a titanium stabilized steel as a function of ageing time. We have therefore used atom-probe field-ion microscopy to follow the compositional changes of MC particles in such a steel during static ageing at 700 and 750° C. The steel investigated was indentical to one of those studied by Thorwaldsson and Dunlop [1, 3]. The carbide particles were approximately 10 nm in size, and they were analysed, atom by atom, using time-of-flight atom-probe spectrometry.

In the atom-probe instrument, specimen surface atoms are removed by pulsed field evaporation. The mass-to-charge ratio (m/q) of each resulting ion is then computed from its flight time and the evaporating voltage. A detailed description of the technique can be found in the review by Müller and Tsong [4]. The atom-probe technique is well suited for the analysis of small precipitates, and several investigations of various steels containing small carbides [5–9] and nitrides [5, 10, 11] have been made using atom-probe microanalysis.

2. Experimental procedure

2.1. Material treatment

The alloy, which was prepared in a vacuum induction furnace by Uddeholm AB, had the following composition (wt%): 0.11 C, 17.1 Cr, 12.6 Ni, 0.49 Ti, 0.50 Si, 1.50 Mn, balance Fe. After forging and hot rolling to a 10 mm × 30 mm bar the material was solution treated at 1250° C for 15 min and water quenched. Bars of 10 mm square cross-section were then cut and given a 5% cold deformation to provide a suitable dislocation density for the nucleation of the MC particles. Finally, the bars were cut into slices, about 1 mm in thickness, which were aged in sealed silica capsules at 700 or 750° C for times ranging from 3 to 1170 h.

2.2. Atom-probe field-ion microscopy

Pins cut out from the heat treated material were electropolished to field-ion specimen tips using the floating layer technique. A transmission electron
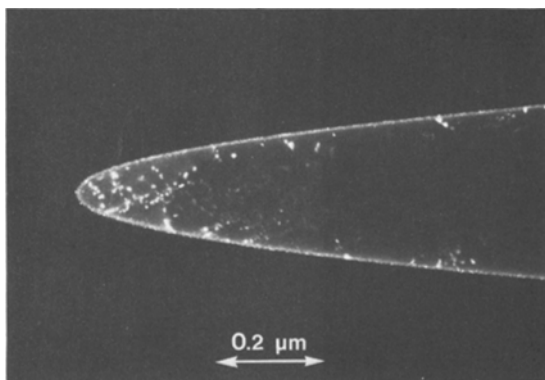
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Figure 1 Stainless steel specimen tip as polished. MC particles, approximately 8 nm in size, have precipitated primarily on dislocations. 100 kV dark field transmission electron micrograph, using a carbide reflexion.

micrograph of a polished specimen is shown in Fig. 1. Carbide particles have precipitated primarily on dislocations during the ageing treatment.

The atom-probe field-ion microscope used for this investigation has been described elswhere [12]. The stainless steel specimens were field-ion imaged at 92 K, and due to the high concentration of alloying elements the field-ion image of the matrix looks almost random. The carbide precipitates image brighter than the matrix (Fig. 2).

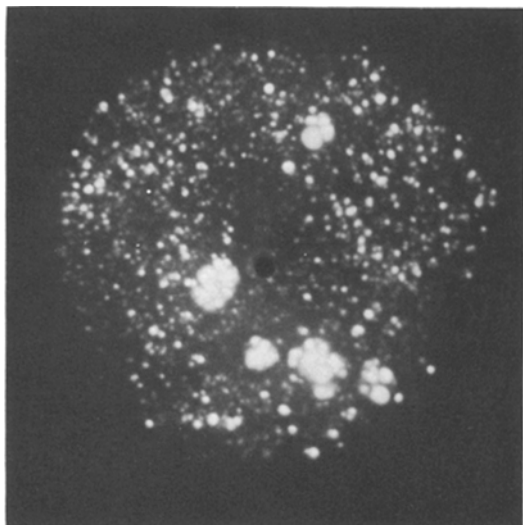Atom-probe analyses were carried out in vacuum

Figure 2 Field-ion micrograph of a stainless steel specimen. Due to the higher evaporation field and smaller radii of the carbide particles, they are imaged brighter and with about 25% higher magnification than the matrix. Before analysis, the specimen is tilted so that the image of a particle falls on the probe hole (centre). 8.6 kV neon micrograph; diameter of probed area approximately 5 nm.

(with a pressure of less than 7.5×10^{-10} torr or 100 nPa) at 92 K. A typical mass spectrum obtained from a particle is shown in Fig. 3. Peaks from singly and doubly ionized carbon, as well as from Ti^{2+} and Ti^{3+} are easily identified. A large peak from Cr^{2+} shows that a considerable amount of chromium is present in the particle. The absence of iron (dominant peak expected at $m/q = 28$) and nickel (largest peak at $m/q = 29$) shows that the chromium atoms recorded indeed come from the particle and not from the matrix. Minor peaks at $m/q = 18$ and 36 frequently occur during carbide analysis, (but never when analysing the matrix), and these peaks are interpreted as C_3^{2+} and C_3^{+}. Sometimes also a few counts at $m/q = 25.5$ are seen. These are due to V^{2+}; vanadium was not intentionally added to the alloy but is present as an impurity (to about 0.01 wt%).

3. Results

Two to five particles were analysed for each of the five ageing treatments studied (3, 24, 169 and 1130 h at 700° C, and 1170 h at 750° C). The particles were between 8 and 14 nm in size and, in all, about 3000 ions were recorded during the analyses. Of all these ions recorded, 14 were identified as iron and 5 as nickel. These ions were assumed to stem from the matrix, and were omitted from the analyses together with the proportional number of 3 chromium ions. The resulting analyses are summarized in Table I. To estimate the uncertainties in the measured values due to the finite number of ions recorded, the usual Gaussian approximation was made. In Table I, ± 2 standard deviation limits are given, which correspond to a confidence level of approximately 95%.

All of the particles analysed were found to contain chromium. At 700° C, the chromium content decreased with increasing ageing time from about 14 at% after 3 h to 5 at% after 1130 h, see Fig. 4. The chromium content, after ageing at 750° C for 1170 h, of 11.5 at%, was significantly higher than the corresponding chromium concentration at 700° C (points to the right in Fig. 4). At 700° C the carbon content increased with ageing time, reaching an approximately stoichiometric particle composition after 1130 h. On the other hand, ageing for 1170 h at 750° C resulted in a significant carbon deficit. The lowest carbon concentration that was measured 39.2 at%, corresponds to the formula $MC_{0.64}$.
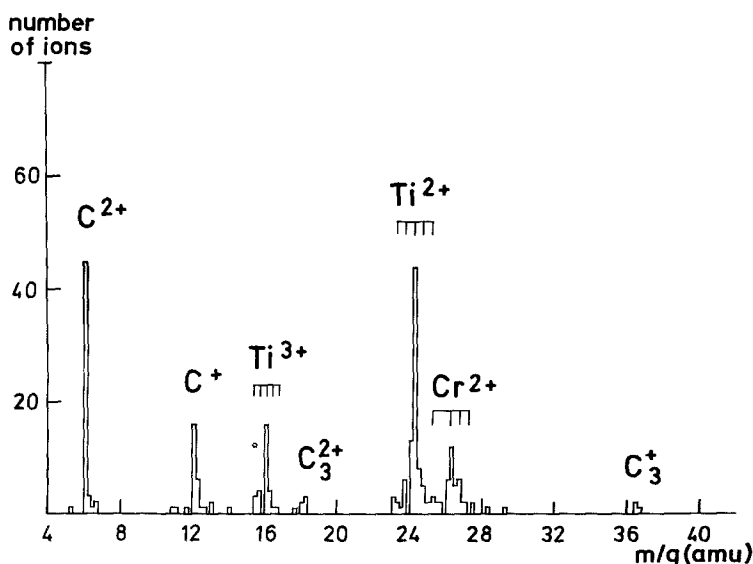
4. Discussion

The particles and the matrix were always found to have a parallel orientation (i.e. $\{111\}_{MC}//\{111\}_\gamma$ and $\langle 110 \rangle_{MC}//\langle 110 \rangle_\gamma$) when the specimen tips were examined in the electron microscope. The lattice parameter of TiC ($a = 0.433$ nm) is approximately 20% larger than that of the matrix ($a = 0.360$ nm) The simple criterion that a particle, n atomic planes in size, is fully coherent with the matrix only when $n \, d_{part} < (n+1) \, d_{matrix}$ (where d_{part} is the interplanar spacing for the particle and d_{matrix} is the corresponding interplanar spacing for the matrix), suggests that the particles studied, 8 to 14 nm in size, were semi-coherent.

It is known that the lattice parameter of TiC decreases both with decreasing carbon content and when titanium is replaced by chromium. Extrapolating the X-ray diffraction lattice parameter data by Rassaerts *et al.* [13], the 14 at% chromium and 40 at% carbon concentrations measured after ageing for 3 h at 700° C correspond to a lattice

parameter $a = 0.428$ nm, or a lattice contraction of about 1% relative to pure TiC.

4.1. Ageing at 700° C

Available diffusion data show that the diffusion distances of chromium and carbon at 700° C are already well over one particle diameter after 3 h $\{(Dt)^{1/2} = 30$ nm for Cr and 25 μm for C [14, 15]$\}$. Consequently the MC particles should be able to adjust their chromium and carbon content during growth so that their free energy is minimized at all times. If the lattice parameter of MC particles after short ageing times (3 hours at 700° C) is smaller than that of pure TiC, then the difference between particle and matrix lattice parameters, $a_{MC} - a_\gamma$, is reduced by about 5%. Assuming that the free energy of the particle-matrix interface increases linearly with the interfacial dislocation density, and assuming this density to be proportional to $a_{MC} - a_\gamma$, the interfacial energy is then lowered by about 5%. This reduction in

TABLE I Atom-probe analyses of 15 MC particles from 5 different ageing treatments. For each treatment the sum of the individual particle analyses is given. In the compositions given, the isotope overlap $_{50}$Ti + $_{50}$Cr has been corrected for. The error limits represent two standard deviations.

Ageing time (h)	Ageing temp. (°C)	Number of particles analysed	Number of ions recorded				Particle composition (at%)		
			C	Ti(+ V)*	Cr	Total	C	Ti(+ V)	Cr
3	700	4	280	321	91	692	40.5 ± 3.7	45.8 ± 3.8	13.7 ± 2.6
24	700	2	304	385	87	776	39.2 ± 3.5	49.1 ± 3.6	11.7 ± 2.3
169	700	2	275	290	49	614	44.8 ± 4.0	46.9 ± 4.0	8.3 ± 2.2
1130	700	5	290	258	28	576	50.3 ± 4.2	44.6 ± 4.1	5.1 ± 1.8
1170	750	2	129	153	35	317	40.7 ± 5.5	47.8 ± 5.6	11.5 ± 3.6

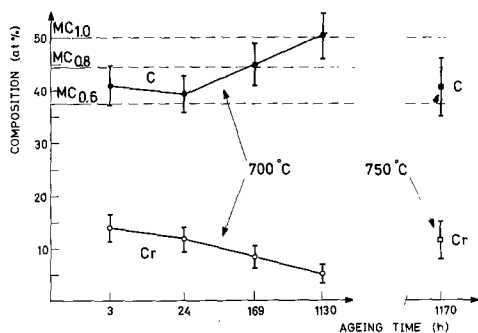* including the isotope $_{50}$Cr

Figure 4 Average particle composition as a function of ageing time.

interfacial energy must then exceed the accompanying increase in volume free energy due to the non-equilibrium composition. As the particles grow during ageing, the relative importance of the volume energy increases, resulting in a gradual decrease in the chromium concentration and an increase in the carbon concentration. After 1130 h of ageing only 5 at% chromium remains, and the carbon content has grown so that stoichiometric proportions are approached.

4.2. Ageing at 750° C

From the material aged at 750° C, only that which had been aged for 1170 h was studied. The chromium content of the MC particles was found to be significantly higher and the carbon content found to be lower than was observed in particles aged at 700° C for about the same time.

The eutectic temperature of the (pseudo-binary) system TiC–Cr is about 1100° C [16], so it may be expected that the solubility of chromium in TiC is somewhat higher at 750° C than at 700° C, but the effect of this increased solubility on particle composition should be rather small.

As mentioned above, Thorwaldsson and Dunlop [1, 3] observed that MC precipitates in this steel become unstable relative to $M_{23}C_6$ after long ageing times (over 1000 h) at 750° C. As the MC particles dissolve, their growth sequence should be reversed so that their chromium content increases. An alternative explanation for the observed high chromium content would then be that the particles analysed were dissolving rather than growing. Analyses from more ageing times are needed to investigate whether this explanation is correct.

5. Conclusions

1. MC precipitates in a titanium stabilized austenitic stainless steel have been analysed using atom-

probe field-ion microscopy. All of the precipitates which were analysed were found to contain significant amounts of chromium.

2. The composition of MC varies with time on ageing at 700° C. The chromium content gradually decreases from 14 at% at 3 h to 5 at% at 1130 h.

3. During this same period the carbon content increases from 40 at% to 50 at%.

4. Ageing for 1170 h at 750° C produced MC precipitates containing 12 at% chromium and 41 at% carbon.

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