Comments on *Small-angle neutron scattering analysis of the precipitation behaviour in a maraging steel* by Staron, Jamnig, Leitner, Ebner & Clemens (2003)

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Further to the paper by Staron, Jamnig, Leitner, Ebner & Clemens [*J. Appl. Cryst.* (2003), **36**, 415–419], the following points are made. Characterization of the precipitation process in maraging steels is difficult, primarily because the precipitates formed are on the nanometre scale. Identification of the precipitate type is complicated by the fact that its composition evolves during ageing, even when the precipitate type remains unchanged. Interpretation of experimental results should be treated with caution, especially when indirect methods, such as small-angle neutron scattering (SANS), are used. Atom-probe field ion microscopy (APFIM) has proved to be capable of determining the type and composition of the fine precipitates in maraging steels. The advantages and disadvantages of SANS and APFIM are briefly discussed.

1. Introduction

A generic class of ultra-high strength maraging steels has been developed over the past 40 years, mainly for aircraft, aerospace and tooling applications. The ultra-high strength is due to precipitation, usually of intermetallic compounds, during the ageing process (Floreen & Decker, 1979; Decker & Floreen, 1988; Vasudevan *et al.*, 1990; Sha *et al.*, 1993*a,b,c,d*; Guo *et al.*, 2003). Characterization of the precipitates is difficult, primarily due to their fine size, which is usually on the nanometre scale. A variety of techniques have been employed to study the type, composition, size and volume fraction of the precipitates formed in maraging steels. These include direct methods, such as transmission electron microscopy (Vasudevan *et al.*, 1990) and atom-probe field ion microscopy (Sha *et al.*, 1993*a,b,c,d*; Guo *et al.*, 2003), and indirect methods, such as small-angle X-ray scattering (Tewari *et al.*, 2000), small-angle neutron scattering (Servant & Bouzid, 1989) and Mössbauer spectroscopy (Li & Yin, 1995). Recently, Staron *et al.* studied the precipitation behaviour in a Cr-containing maraging steel using energy filtering transmission electron microcopy (EFTEM) and small-angle neutron scattering (SANS) (Staron *et al.*, 2003). Their analyses of the experimental results led to the conclusion that the precipitates formed are solely the intermetallic G-phase, $Ti_6Si_7Ni_{16}$, with none of the Ni_3Ti type. This is in contradiction with what was reported by Gemperle and Sha *et al.* (Gemperle *et al.*, 1992; Sha *et al.*, 1993*c*), who studied virtually the same alloy using atom-probe field ion microscopy (APFIM) and observed the existence of both Ni_3Ti and the $Ti_6Si_7Ni_{16}$ G-phase. Formation of reverted austenite was also observed when the alloy was over-aged. The aim of this communication is to reveal what may be responsible for the above discrepancies. The advantages and disadvantages of SANS and APFIM are briefly discussed.

2. Discussion

The alloys studied by Gemperle *et al.* and Staron *et al.* are slightly different in composition, as shown in Table 1. Such a difference, however, is not expected to alter the precipitation behaviour of the alloys much. In the work by Staron *et al.*, qualitative information about the composition of the precipitates was provided by the EFTEM mapping images of various elements. They then claimed that all precipitates are of one type, showing depletion in Fe and Cr and enrichment in Ni, Ti and Si. However, such a qualitative approach may result in misleading conclusions. On the one hand, it is virtually impossible to tell that depletion or enrichment of various elements indeed takes place at each precipitate, especially when the precipitates studied are on an extremely fine scale and of a high number density. On the other hand, it is possible that precipitates of different types may be adjacent, one type being the nucleation site of another type (Stiller *et al.*, 1996, 1998). Murayama *et al.* reported that fine particles of G-phase, enriched in Si, Ni and Mn, have been found in intimate contact with the Cu precipitates in a PH17-4 stainless steel (Murayama *et al.*, 1999). The subtle position difference of such precipitates of different types may not be discernible for EFTEM. The EFTEM mapping images do not provide enough evidence to discard the existence of Ni_3Ti precipitates.

There is indeed another reason for Staron *et al.* to exclude the possible presence of Ni_3Ti. The calculated nuclear scattering length density (NSLD) and the ratio A of magnetic to nuclear scattering intensity for Ni_3Ti deviate from the values measured by SANS. However, a closer look at their calculations reveals that some of the assumptions used can be improved.

Table 1
Chemical composition of the Cr-containing steels (at.%).

	C	Al	Cr	Mo	Ni	Ti	Si	Mn	Fe
Gemperle *et al.* (1992)	0.1	1.2	11.2	1.3	9.1	1.0	1.0	0.2	Balance
Staron *et al.* (2003)	0.05	1.2	13.0	0.6	8.3	1.0	1.1	0.1	Balance

Firstly, the precipitate formed was assumed to be of stoichiometric composition in their calculations. In reality, the composition of a certain type of precipitate evolves during ageing and it may deviate significantly from the stoichiometric formula (Guo *et al.*, 2003; Guo & Sha, 2002). Since the calculation of the NSLD and *A* is very sensitive to the phase composition, the calculated NSLD and *A* values may not be accurate. If the composition of Ni_3Ti measured by APFIM, *i.e.* Fe–2Cr–2Mo–65Ni–7Al–20Ti (at.%) after 5 h at 793 K, is used, the calculated values for η_{nuc} and *A* will be 5.68×10^{14} m^{-2} and 7.44, respectively. If the ageing is carried out at lower temperatures for a shorter time, the NSLD and *A* values calculated from the real composition may fall within the range of the measured values. In fact, if one looks closely at the volume fraction of precipitates formed (Table 3 in Staron *et al.*), one will realise that whatever type the precipitate is, $Ti_6Si_7Ni_{16}$, Ni_3Ti or Ni_3Mo, the alloy composition simply does not allow such high amounts of precipitates to form. The formation of 7.8 mol% (mol% very close to vol% in numerical values) $Ti_6Si_7Ni_{16}$ requires about 1.6 mol% Ti and 1.9 mol% Si, whereas the alloy only contains 1.0 mol% Ti and 1.1 mol% Si. Indeed, Staron *et al.* did realise that the composition could change with time but probably they underestimated the extent of its influence.

Secondly, the composition of the matrix is assumed to be unchanged prior to and after ageing, which cannot be justified. If the martensite matrix composition after 5 h at 793 K is used, *i.e.*, Fe–0.7Si–11.4Cr–1.1Mo–2.8Ni–0.5Al–0.1Ti (at.%), the calculated NSLD value for $\eta_{nuc, m}$ would be 7.39×10^{14} m^{-2}, instead of 7.24×10^{14} m^{-2}. In turn, the calculated *A* ratio for Ni_3Ti is 6.3 ($\eta_{nuc} = 5.68 \times 10^{14}$ m^{-2}), whereas the calculated values for η_{nuc} and *A* for the G-phase are 4.87×10^{14} m^{-2} and 3.5, respectively. It is not clear what role the reverted austenite will play in the calculations. The austenite formed during ageing has a composition different to that of the parent martensite. It can be considered as a precipitate and is sometimes termed precipitated austenite. Its existence after long-term ageing is a matter of fact, which contributes very much to the softening of maraging steels after peak hardness. A comparison of the newly calculated values and those reported by Staron *et al.* is given in Table 2.

3. Conclusions

From the discussions above, one can see the uncertainties involved in the original SANS analysis by Staron *et al.* Both SANS and APFIM are well established techniques for the study of fine precipitates. Each has its own advantages and disadvantages, and which technique is to be used depends on the purpose of the research. One significant advantage of SANS over TEM and APFIM is that its sampling size can be many orders of magnitude larger, and therefore the inhomogeneity statistics of SANS are more representative of the microstructure sampled. The size distribution and number density of the precipitates formed during early stages, when they are very small, can be determined by SANS. However, interpretation of the SANS results may not be straightforward if there is more than one type of precipitate in the matrix simultaneously (Große *et al.*, 2000). On the other hand, there is little uncertainty in the identification of precipitate type and composition by APFIM, due to its unique capability of measuring composition variations on a nanometre scale, together with equal detection efficiency for all elements. There should be little doubt that the precipitates formed in the Cr-containing steels studied consist of both $Ti_6Si_7Ni_{16}$ G-phase and Ni_3Ti.

Table 2
Calculated nuclear scattering length densities and *A* ratios of some intermetallic coherent precipitates, compared with the values obtained experimentally.

	$\eta_{nuc, p}$ (10^{14} m^{-2})		*A* ratio	
Measured	5.2–5.5		4.6–6.4	
Calculated	Staron *et al.*	New values†	Staron *et al.*	New values†
$Ti_6Si_7Ni_{16}$	5.10	4.87	4.4	3.5
Ni_3Ti	5.86	5.68	9.2	6.3
Ni_2Ti	4.88		3.8	3.5
NiTi	2.93		1.8	1.8
NiAl	5.87		9.3	7.7
Ni_4Mo	8.18		18.8	26.6
Ni_3Mo	8.03		26.4	40.1

† Calculated based on the phase composition after 5 h at 793 K.

In conclusion, atom-probe field ion microscopy has proved to be a powerful tool for studying the precipitation process in maraging steels. It can determine the type, size and composition of the precipitates formed in a straightforward way. The precipitates formed in the Cr-containing maraging steel consist of the $Ti_6Si_7Ni_{16}$ G-phase and the Ni_3Ti phase. Interpretation of SANS results should be treated with caution, especially when little is known about the precipitate types and size.

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