Alloy design of nanoprecipitate-hardened high-Mn maraging-TRIP and -TWIP steels


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Overview

- Introduction
- Compositions and processing
- Mechanical properties and microstructures
- Characterization of precipitations
- Formation of new austenite during aging
- Conclusions
Steel for automotive applications:

Good combination of **strength**, **ductility**, **price**

- Lean Maraging TRIP Steels
  
  - Ductile low carbon martensite matrix
  - Small amount of austenite (TRIP, TWIP)
  - Controlled precipitation hardening
Overview

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  - Mechanical properties and microstructures
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### Compositions in mass%: classical maraging steel

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<tr>
<th>Steel</th>
<th>C</th>
<th>Ni</th>
<th>Co</th>
<th>Mo</th>
<th>Ti</th>
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<td>18</td>
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<td>1.6</td>
<td>0.15</td>
<td>0.05</td>
<td>Balance</td>
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- **Low carbon: ductile martensite**
- **Precipitation hardening**

Expensive for automotive applications!

Optimised for very high strength + toughness

We want high strength + ductility
## Compositions in mass%: new lean maraging steels

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**Low carbon: ductile martensite**

**Precipitation Hardenable**

**Mn (+Ni): austenite (TRIP)**
Processing

Vacuum induction melting

Annealing

Hot deformation

Solution heat treatment

Quenching $\rightarrow$ Martensite $+\text{retained austenite}$

Aging (450°C) $\rightarrow$ “Maraging“ $\text{retained} + \text{new austenite}$
Overview

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- **Mechanical properties and microstructures**
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Hardness during aging at 450°C

**Vickers hardness HV5**

Time at 450°C (min)

- 09MnPH
- 12MnPH
- 15MnPH

12MnPH after aging (48h 450°C)

precipitates in $\alpha'$

$$x_{Diff} \approx 2\sqrt{Dt} \approx 30\text{nm}$$

no precipitates in austenite

$$x_{Diff} \approx 2\text{nm}$$
Tensile tests

Ni-Maraging

(X3NiCoMoTi18-12-4)

12MnPH

Ni-Maraging (450°C/48h)

12MnPH (450°C/48h)

Engineering Stress (MPa)

Engineering Strain (%)

0 5 10 15 20 25

Engineering Stress (MPa)

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Engineering Strain (%)

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Ni-
Maraging

12MnPH

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**Atom Probe Tomography (APT)**

- **Tip-shaped sample** initiated evaporation by + or ~ 10 kV

- **Counts**
  - Mass to charge ratio

- **3D atom map**

**APT**: Time of flight measurement (chemical identification)

+ Ion projection microscopy (determination of position)
Atom Probe, 12MnPH aged (48h, 450°C)

Fe

Ni $\alpha'$+particles $\gamma$ (no particles)

Mn enrichment in interface?

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09MnPH aging at 450°C, Proxigrams

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09MnPH
450°C/48h

matrix ⇐⇒ particle

09MnPH
450°C/192h

matrix ⇐⇒ particle

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### Chemical compositions (09MnPH; 450°C/48h)

<table>
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<tr>
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<th>at. % in particles</th>
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<tbody>
<tr>
<td>Ni</td>
<td>39.99</td>
<td>52.88</td>
</tr>
<tr>
<td>Mn</td>
<td>24.70</td>
<td>32.66</td>
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<tr>
<td>Al</td>
<td>7.02</td>
<td>9.28</td>
</tr>
<tr>
<td>Ti</td>
<td>3.91</td>
<td>5.17</td>
</tr>
<tr>
<td>Fe</td>
<td>23.97</td>
<td>0</td>
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possible: $\text{Ni}_{50}(\text{Mn, Al, Ti})_{50}$

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TEM results (09Mn PH after 192h/450°C)

Particle: $a = 0.280 \pm 0.006\text{nm}$ (assuming bcc structure)
Matrix: $a = 0.275 \pm 0.003\text{nm}$
### 09MnPH aging at 450°C

#### Aging time at 450°C

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<th>192 hours</th>
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<tr>
<td>Volume fraction of particles</td>
<td>1.5%</td>
<td>4.3%</td>
</tr>
<tr>
<td>Number density of particles (m⁻³)</td>
<td>3.6x10²⁴</td>
<td>1.9x10²⁴</td>
</tr>
<tr>
<td>Mean diameter (nm)</td>
<td>4.7 ± 0.7</td>
<td>6.1 ± 2.2</td>
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#### Iso-conc. surfaces:
- 14 at.% Ni
- only Fe and Ni shown

![Image of aged samples](image_url)
09MnPH (48h, 450°C)

⇒ Precipitation volume fraction $f$ about 1.5%
Mean diameter $d = 4.7 \text{ nm} \ (± \ 0.7 \text{ nm})$

Assuming dislocations bypassing particles (Orowan looping):

$$\sigma_{OR} \approx \frac{MGb \sqrt{f}}{r}$$

$$\sigma_{OR} \approx \frac{3 \cdot 80 \text{GPa} \cdot 0.248nm \cdot \sqrt{0.015}}{2.35nm} = 3100\text{MPa}$$

From experiment:
ΔYS: ~300MPa

Shearable coherent particles ?
Cutting of particles (Friedel cutting) ?

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Assuming dislocations bypassing particles (Orowan looping):

Mean diameter \(d = 4.7 \text{ nm} \pm 0.7 \text{ nm}\)

\[ \Rightarrow \text{Precipitation volume fraction} \ (f) \approx 1.5\% \]

From experiment:

\(\text{DYS:} \sim 300 \text{ MPa} \) 

\[\text{09MnPH (48h, 450° C)}\]

Shearable coherent particles? 

Cutting of particles (Friedel cutting)?

After aging (48h 450°C) nanosized precipitations in martensite 
(Ø ~ 5nm; volume fraction ~ 1.5%)

Heusler Alloy (Ni$_2$MnAl)? B2 or L2$_1$? Coherent? 
Cut by dislocations?
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Effect of aging on ductility

12MnPH

12 wt.% Mn, 0.01 wt.% C, 2 wt.% Ni, 1 wt.% Ti, 0.15 wt.% Al, 1 wt.% Mo, 0.06 wt.% Si

TRIP effect (austenite transforms to martensite)

Maraging effect (precipitation hardening in martensite)

D. Raabe, D. Ponge, O. Dmitrieva, B. Sander, Scripta Mater. 60 (2009) 1141
Effect of aging on ductility

- **as-quenched**
- **aged 450°C/48h**

- Increase of austenite fraction during aging

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**Engineering Stress (MPa)**

**Engineering Strain (%)**

- **α-Fe (Martensite)**
- **γ-Fe (Austenite), vol. fraction 15-20%**
Effect of aging on ductility

**Engineering Stress (MPa)**

- as-quenched
- aged 450°C/48h

**Engineering Strain (%)**

1. strain 0%
2. strain 15%

**Precipitation hardening**

- Increase of austenite fraction during aging

**Phase Identification**

- α-Fe (Martensite)
- γ-Fe (Austenite), vol. fraction 15-20%

**Chemical Composition**

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Effect of cold rolling after aging

~40% γ in equilibrium at 450°C (Thermocalc)

γ → α’ (TRIP)

γ formation during aging
450°C/48h

-aged (450°C/48h)

quenched

12MnPH X-Ray
APT results: Atomic map (12MnPH aged 450°C/48h)

**Mn atoms, Ni atoms**

**Mn iso-conc**: 18 at.%

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70 million ions
Laser mode (0.4nJ, 54K)

Martensite decorated by precipitations

Austenite?
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**Design of “Lean Maraging TRIP steel“**

- Precipitation hardening ➔ Increase strength
- Austenite (retained + new) ➔ Increase ductility

- Martensitic Mn-steels (~0.01 wt% C): good ductility

- + controlled amounts of Ni (2 wt%), Al (0.15 wt%), … increase strength during aging by formation of nanosized precipitations without significant reduction of ductility

- By controlling the austenite stability (here by Mn) martensite can be refined and ductility can be further increased by retained and reverted austenite (TRIP)