σ-Phase, its Properties and its Relevance to Stainless Steels

Stanislaw M. Dubiel
AGH University of Science & Technology, Krakow, Poland
Stainless Steel History

- Must contain $\geq 10.5\%$ Cr and low content of carbon

- Discovered in 1900 – 1915 as effort of investigations of many people; Leon Guillet (F), Giesen (GB), Harry Brearley (GB), Philip Monnartz (D), Portevin (F), Borchers (D) and Max Mauermann (PL)

1912: English metallurgist Harry Brearley invents SS in his search for an alloy to protect cannon bores from erosion. The first commercial production of SS occurs in August, 1913.

1915: During World War I, SS is used to manufacture valves for aircraft engines.

1919-1923: Sheffield cutlers start regular production of SS cutlery, surgical scalpels and tools.

1924: The first SS roof makes an appearance in America.

1928: The brewery industry installs the first SS fermenting tank.
1929: The first SS tanker is used for transporting 3,000 gallons of milk.

1929-1930: The Chrysler Building’s top seven arches are clad in SS. This New York City landmark is one of the world’s most recognized skyscrapers.

1931: The first SS railway carriage appears in the US. Also, Rolls Royce produces the first SS radiator grill and emblem.

1933: SS kitchen sinks and furniture are introduced.

1950: SS is used with increasing frequency for car accessories.

1954: The first SS underwater TV camera is made.

1963: The first SS razor blades are produced.

1969: The first men on the moon (Apollo 11) are taken there by a SS Saturn V Rocket.

2000: Grey Feather Toy Creations introduces bird toys constructed exclusively with SS
STAINLESS STEELS FAMILY

• Austenitic and Super Austenitic SS (grades: 304, 316, 321, 347); typically: \(18\%\text{Cr}\) and \(10\%\text{Ni}\), known also as 18/10 SS (70% of all SS)

• Duplex and Super Duplex SS 50/50 mix of ferrite and austenite (grades: 2205, 2324, 2327, 2328, 2377); \(19\text{-}28\%\text{Cr}, 7\%\text{Ni}\) and \(\leq 5\%\text{Mo}\)

• Ferritic SS; \(10\text{-}29\%\text{Cr}\), few % of Mo, W, Ni (Fe-29Cr-4Mo; Fe-29Cr-4W;Fe-29Cr-2Ni)

• Martensitic SS; \(12\text{-}14\%\text{Cr}\), \(\leq 2\%\text{Ni}\), \(\leq 1\%\text{Mo}\)
Increase from ~16 to ~27 mmt (~75 bln $)
EXAMPLES OF INDUSTRIAL USE

• Oil Refineries and Pipelines
EXAMPLES OF INDUSTRIAL USE

• Power Plants, Heat Exchangers
  Gas Turbines and Boilers
EXAMPLES OF INDUSTRIAL USE

• Buildings and Constructions
EXAMPLES OF INDUSTRIAL USE

- Motobikes, Cutlery and Watches
THE PROBLEM

Precipitation of the $\sigma$-phase that causes degradation of many useful properties

- decrease of ductility and impact toughness
- increase of embrittlement
- decrease of corrosion resistance
- increase of hydrogen-induced embrittlement and cracking
PRECIPITATION

Mater. Charact., 59 (2008) 503; superferric SS (Fig.1); duplex SS (Figs. 5-7)
FAILURES & LEAKAGES
SIGMA - PHASE FAMILY

- 53 cases in binary alloys e.g. FeCr, FeNb, FeTa, FeV, FeMo, FeTc, FeRe
PHASE DIAGRAM - FeV SYSTEM

- Liquid
- 1910°C
- 1538°C
- 1394°C
- 1321°C
- 912°C
- 46.5% V
- α
- γ
- α + σ
- σ
- α + σ

TEMPERATURE_CELSIUS vs WEIGHT_PERCENT V
<table>
<thead>
<tr>
<th>No</th>
<th>Site</th>
<th>CN</th>
<th>ON</th>
<th>&lt;d&gt;[nm]</th>
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<tr>
<td>1</td>
<td>I/A</td>
<td>12</td>
<td>2</td>
<td>0.2508</td>
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<tr>
<td>2</td>
<td>II/B</td>
<td>15</td>
<td>4</td>
<td>0.2701</td>
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<tr>
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<td>8</td>
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<tr>
<td>5</td>
<td>V/E</td>
<td>14</td>
<td>8</td>
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</table>
• Mössbauer spectroscopy ($\sigma$-FeCr) $B_a = 13.5$ T

Five different sites occupied by Fe atoms

J. Cieslak, M. Reissner, S. M. Dubiel, W. Steiner, PSS(a), 205 (2008) 1794
STRUCTURE – SITES OCCUPANCY

• Neutrons (σ-FeCr and σ-FeV)

IDENTIFICATION OF SIGMA

\[ \Delta IS = IS_\sigma - IS_\alpha \approx -0.1 \text{ mm/s} \approx 0.05 \text{ e} \]
TRANSFORMATION KINETICS

- $\sigma$-FeCr; Isothermal annealing at $\sim 530 \leq T_a \leq \sim 830^\circ C$

Johnson-Mehl-Avrami equ.

\[ E = 196 \pm 2 \text{ kJ/mol} \]
DEBYE TEMPERATURE

- $\sigma$-FeCr \quad 4.2 \, \text{K} \leq T \leq 60 \, \text{K}
DEBYE TEMPERATURE

$$\Theta_D(\text{Cr}) = 630 \text{ K}$$

$$\Theta_D(\text{V}) = 380 \text{ K}$$

![Graph showing Debye temperature as a function of at% V, Cr]
CURIE TEMPERATURE

- Mössbauer effect (σ-FeCr)

(a) \( x = 45.0 \), (b) \( x = 46.2 \) and (c) \( x = 48.0 \)

(a) 4.2 K; (b) 295 K

CURIE TEMPERATURE

- Mössbauer effect ($\sigma$-FeV$_{34}$)

$T_c = 323$ K

CURIE TEMPERATURE

- Magnetization vs. $T$ - $\sigma$-FeV$_x$

$X = 34.4$
$X = 39.9$
$X = 47.8$
CURIE TEMPERATURE

\[ \sigma-\text{FeV} \]

\[ \sigma-\text{FeCr} \]

\[ RT \]

\[ T_c [K] \]

\[ x \text{ [at\%]} \]
MAGNETIC MOMENT

- Magnetization vs. $B_a$ - $\sigma$-FeV
MAGNETIC MOMENT

- $\sigma$-FeV$_x$
B - $\mu$ RELATIONSHIP

\[ \langle B \rangle \text{ [T]} = 12 \times \langle \mu \rangle \text{ [$\mu_B$]} \]

- $\sigma$-Fe$_{100-x}$Cr$_x$
- $\sigma$-Fe$_{100-x}$V$_x$
COPULING CONSTANT, A

A (T/uB)
MAGNETISM OF SIGMA

- Rhodes-Wohlfarth plot

4K $\sigma$-FeCr

Itinerant character of magnetism
CONCLUSIONS

• Sigma-phase in Fe-Cr and Fe-V based alloy systems can be quantitatively studied by MS

• Following characteristics relevant to the phase can be investigated:
  ▶ Its identification and determination of relative amount
  ▶ Determination of the transformation kinetics
  ▶ Determination of the Curie and Debye temperatures
Acknowledgement

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- Walter Steiner, TU, Wien
- Jakub Cieslak, AGH, Krakow
Thank you for your attention

The 1st oil refinery in the world (1856), Ulaszowice (Galicia, Poland)
$\sigma$-FeCr$_{46.2}$ at RT
SPECTRAL PARAMETERS

## SPECTRAL PARAMETERS

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<tr>
<th></th>
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<tbody>
<tr>
<td></td>
<td>Prob. %</td>
<td>IS* mm/</td>
<td>QS mm/</td>
</tr>
<tr>
<td>A</td>
<td>11.3</td>
<td>$0.27$</td>
<td>$0.34$</td>
</tr>
<tr>
<td>B</td>
<td>6.4</td>
<td>$0.07$</td>
<td>0.24</td>
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<tr>
<td>C</td>
<td>20.5</td>
<td>$-0.24$</td>
<td>0.18</td>
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<tr>
<td>D</td>
<td>44.9</td>
<td>$-0.06$</td>
<td>0.21</td>
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<tr>
<td>E</td>
<td>17.0</td>
<td>$-0.17$</td>
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* Relative to bcc-Fe