Copper-precipitation hardening in a non-ferromagnetic face-centered cubic austenitic steel

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Copper additions are utilized for precipitation hardening of a non-ferromagnetic austenitic face-centered cubic (fcc) steel. Additions of up to 25 wt.% Mn, 15 wt.% Ni, 6 wt.% Cu, and 0.6 wt.% C are found to stabilize austenite sufficiently to prevent transformation to either \(\alpha'\)- or \(\varepsilon\)-martensite upon heavy mechanical deformation up to 75% reduction in thickness, with the alloys remaining paramagnetic. Mechanical properties are characterized and the tensile strength (447 MPa) is correlated with copper-precipitation as revealed directly by local-electrode atom-probe tomography.

Keywords: Precipitation hardening; Atom-probe tomography; Non-ferromagnetic fcc austenitic Steels; Copper-precipitation

Non-ferromagnetic steels are of interest for applications such as non-ferromagnetic tools. Austenitic 18 wt.%Cr–8 wt.%Ni stainless steels are non-ferromagnetic if rapidly cooled from the stable fcc austenitic phase field, but they transform to ferromagnetic martensite upon cold working. Chromium is added to austenitic steels primarily for corrosion resistance but it does not thermodynamically stabilize the fcc phase. We investigate Mn, Ni, Cu, and C additions for stabilization of the fcc phase. All of these elements stabilize the austenitic phase [1,2]. According to the phase diagrams given in Refs. [3,4], alloys with 25 wt.% Mn and approximately 0.59 wt.% C are fully austenitic. These alloys show intense twinning after mechanical deformation, but do not transform to either tetragonal \(\alpha'\)- or hexagonal \(\varepsilon\)-martensite [3,4]. Therefore, 25 wt.% Mn and 0.59 wt.% C are chosen as a constant base composition. Nickel is added for additional stabilization of austenite. Minimizing the Ni addition is, however, advantageous because of its cost and because it increases the magnetic moment per atom in a ferromagnetic alloy. Copper additions serve both for precipitation strengthening and for additional stabilization of the austenite phase. Both the Ni and Cu concentrations were varied. Austenite stability is evaluated by testing for the presence of ferromagnetism, and structural analyses were performed utilizing X-ray diffraction. Precipitation of Cu-rich precipitates is studied by age-hardening and atom-probe tomography experiments.

Ingots containing 25 wt.% Mn, 5, 10, or 15 wt.% Ni, 0, 2, 3, or 6 wt.% Cu, 0.59 wt.% C, with the balance being Fe, Table 1, were prepared by arc-melting in a protective argon atmosphere. Each ingot weighed about 15 g and they were melted from pure elements and a 1095 grade steel containing nominally 0.95 wt.% C. Each ingot was remelted at least five times to ensure homogeneity. Slices of the ingots were cold rolled to approximately 75% reduction in thickness without intermediate annealing, thereby demonstrating that the alloys were very ductile, at least at room temperature. Subsequently they were solutionized at 950 °C for 0.5 h in air and water quenched. To determine the optimal temperature and time window for precipitation hardening, isochronal aging experiments were performed using a 2 h aging time for temperatures between 500 and 700 °C in 50 °C increments; precipitation was monitored using Vickers microhardness measurements. At 700 °C, peak hardness was observed for 1–2 h aging, Figure 1. The phases present were determined utilizing X-ray diffraction, and Mössbauer spectroscopy was used to study the magnetic properties of the steel. Not all experimental methods were applied to all alloys and...
aging states. The limited amount of steel available permitted one compressive test on Alloy D, employing a cylindrical specimen (5.08 mm diameter and 12.7 mm long) to determine the yield strength and work hardening of the steel with the best combination of mechanical properties among the alloys investigated. Local-electrode atom-probe (LEAP™) tomography [5,6] was employed to reveal nanometer-sized precipitates [7] in Alloy D after aging at 700 °C for 2 h. The LEAP tomographic analyses were performed at a specimen temperature of 80 ± 0.5 K, using 0.6 nJ picosecond laser pulses at a pulse repetition rate of 250 kHz.

Isochronal aging for 2 h produces only gradual increases of the Vickers microhardness for temperatures up to 650 °C for any of the alloys. Isothermal aging at 700 °C generates, however, a distinct Vickers microhardness increase in the alloys containing Cu, with the peak microhardness occurring between 1 and 2 h of aging. The largest microhardness increase is observed for Alloy D, which has the highest copper concentration, 6 wt.% Cu, Figure 1. Both Alloys C and G (3 wt.% Cu) display a distinct microhardness peak but with a smaller amplitude than Alloy D. The correlation of increasing peak microhardness with increasing copper concentration indicates indirectly that Cu precipitation hardening is occurring.

The stress–strain curve for Alloy D, in compression, employing a strain rate of 10⁻³ s⁻¹ at room temperature, after aging for 2 h at 700 °C, is displayed in Figure 2. The 0.2%-offset yield stress is 447 MPa (64 ksi). This alloy exhibits substantial work hardening with a slope of 3094 ± 2 MPa in the linear range between 0.04 and 0.10 engineering strain.

The crystallographic structure after cold rolling was investigated by X-ray diffraction to test whether the austenitic structure of the steel is metastable; that is, if austenite transforms upon mechanical deformation. Figure 3 exhibits the diffractograms for Alloys C, D, F, and G, which differ in their Ni and Cu concentrations. The dominant features in the diffractograms are the large peaks corresponding to the fcc austenite structure (γ-phase), indicating that the alloys are to a large degree austenitic despite severe plastic deformation during cold rolling to a 75% reduction in thickness. Smaller peaks characteristic of the hexagonal ε- and tetragonal α'-martensitic phases are also present in Alloys C, F, and G, indicating the existence of a small volume fraction of ε- and α'-martensite.

It is clear that increasing the Ni concentration from 5 wt.% in Alloy C to 10 wt.% in Alloy F and to 15 wt.% in Alloy G leads to a substantial reduction in the volume fraction of the martensitic phases, thereby making the austenitic phase more stable with increasing Ni concentration. The diffractogram for Alloy D, 5 wt.% Ni and 6 wt.% Cu, does not exhibit peaks characteristic of martensite, reflecting the stabilizing influence of Cu on the austenitic phase.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe (wt.%)</th>
<th>Mn (wt.%)</th>
<th>Ni (wt.%)</th>
<th>Cu (wt.%)</th>
<th>C (wt.%)</th>
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<td>25</td>
<td>5</td>
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<tr>
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<td>25</td>
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<tr>
<td>C</td>
<td>66.41</td>
<td>25</td>
<td>5</td>
<td>3</td>
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<tr>
<td>D</td>
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<td>25</td>
<td>5</td>
<td>6</td>
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</tr>
<tr>
<td>E</td>
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<tr>
<td>F</td>
<td>61.41</td>
<td>25</td>
<td>10</td>
<td>3</td>
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</tr>
<tr>
<td>G</td>
<td>56.41</td>
<td>25</td>
<td>15</td>
<td>3</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Figure 1. Temporal evolution of the Vickers microhardness of Alloys C, D, and G upon isothermal aging at 700 °C, after solutionizing at 950 °C for 0.5 h and quenching into water.

Figure 2. A compressive engineering stress–strain curve of Alloy D, with a strain rate of 10⁻³ s⁻¹ at room temperature; the specimen was initially aged for 2 h at 700 °C and then quenched into water.
Additional evidence for the stability of the austenitic phase in these steels was obtained by Mössbauer spectroscopy of a cold rolled and electrolytically polished thin strip of Alloy E. Only a single peak characteristic of a paramagnetic phase is observed in the Mössbauer spectrum. The absence of the six-line pattern characteristic of a ferromagnetic phase indicates that transformation to ferromagnetic martensite is below the detection limit. An upper limit of 2% of a magnetic phase may, however, possibly be hidden in the spectrum’s noise.

Specimens of Alloy D in the peak microhardness condition, that is, after aging at 700 °C for 2 h, were investigated utilizing a LEAP tomograph to study the nano-sized precipitates causing the observed age-hardening effect. Figure 4 is a 3D atom-by-atom reconstruction of a volume containing copper-rich precipitates. The average radius of the Cu-rich precipitates is 2–2.5 nm at a number density of \((3.4 \pm 0.3) \times 10^{23} \text{ m}^{-3}\). The presence of nanometer-sized Cu-rich precipitates at a high number density in conjunction with the increase in Vickers microhardness demonstrates that copper precipitation can be used for precipitation hardening in austenitic steels, in analogy to ferritic alloys for which it has been utilized and studied thoroughly [8–14].

The proxigram method [8] is used to determine precipitate and matrix compositions, by calculating a concentration profile with respect to distance from the surfaces of the precipitates. The resulting concentration profiles are displayed in Figure 5; the Cu-rich precipitates are on the right-hand side and the fcc matrix on the left-hand side of the diagram.

The proxigram concentration profiles in Figure 5 display a heterophase interfacial region approximately 1–2 nm wide within which the Cu concentration increases to its maximum value of 70 at.% in the precipitate core of the largest precipitates with a 2.5 nm radius. Manganese and C are strongly depleted in the Cu-rich precipitates, and Ni only slightly. There is a heterophase interfacial enrichment of Ni and Mn. This observation is remarkable, since a similar, but more pronounced, segregation effect of Ni and Mn to the heterophase interfaces of Cu-rich precipitates is known to occur for metastable BCC precipitates about 1.5–2.5 nm in radius in BCC ferrite \(\alpha\)-Fe [9–16]. We emphasize that for the alloys studied the Cu precipitates form in the FCC austenite \(\gamma\)-Fe phase and are thus expected to form directly the fcc equilibrium structure of Cu. This result supports the interpretation of segregation in both cases in terms of a Gibbsian interfacial excess that reduces the interfacial free energy between the Fe-rich and Cu-rich phases.

In conclusion, we have demonstrated that a steel with a stable austenitic structure that does not transform to \(\varepsilon\)- or \(\alpha\)-martensite, or \(\alpha\)-ferrite (BCC), and therefore does not become ferromagnetic, is obtained with the composition Fe–25Mn–5Ni–6Cu–0.59C (wt.%). Copious Cu precipitation occurs at 700 °C, causing a substantial precipitation hardening effect observed in both isochronal
and isothermal aging experiments; the hardening effect is due to the formation of nanometer-sized Cu-rich precipitates with 2–2.5 nm diameter, as demonstrated unequivocally by LEAP tomography.

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