Alloy Proposal: Hyper Duplex Stainless Steel

Target Composition: **Fe -28wt%Cr -14wt%Ni -8wt%Mo**

Objective: The composition is based on hyper duplex stainless steels, known for excellent corrosion resistance and high strength. [1] Whilst expensive, they are used for specialist applications such as subsea umbilicals, and tubing for oil wells where higher cost can be justified by significant extension of service life and reduction of maintenance.[4] Maximising salt water corrosion resistance was our main focus when selecting composition, as lower strength can be accommodated through processing or redesign. Corrosion in saltwater occurs primarily through chloride ion attack in pits and crevices; the ability to withstand this process is characterised by the indices Pitting Resistance Equivalent Number (PREN) and Critical Pitting Temperature (CPT) which needs to be over 70°C for the corrosion test.

Alloying additions: Duplex stainless steels contain both austenite (γ) and ferrite stabilising elements. Given the sheer scale of composition space being considered for incorporation, it was determined that in order to narrow selection down and eliminate certain elements, computational methods should be employed. This involved writing an iterative algorithm that would generate ~180,000 permutations of alloy compositions and calculate basic proxy properties including estimated solid solution strengthening, PREN, and cost. Further analysis involved ranking the alloys by scaling the proxies to assign relative weights to each property. In our case, we valued corrosion resistance above all else, followed by strength. The shortlist indicated that corrosion resistance to the extent we were aiming for requires 28wt% Cr and 8wt% Mo.

Chromium forms a passivating layer which is further stabilised by molybdenum [1,2], and these elements are ferrite stabilisers. Molybdenum also greatly elevates PREN by accumulating in pits which hinders further corrosion [2]. Carbon was considered for its enhanced strengthening properties due to Cottrell Atmospheres that pin dislocations; however, in industrial duplex stainless steels, carbon is minimised to avoid carbides, yet, for a small scale ingot and moderate carbon content, heat treatments could be controlled to minimise their formation. Despite this, as the sole γ stabiliser, carbon content would have to far exceed 0.8wt% [7]. Also, if carbides were to form, they could consume significant portions of chromium and molybdenum, severely compromising the corrosion resistance. [3] Nickel was selected as a standard γ stabiliser over nitrogen or carbon as it allows the duplex phase fractions to approach 1:1, although in industrial applications both nickel and carbon could be used.

Exact addition ratios were informed by the following equations and the Schaeffler diagram [1]:

- Cr_{eq} = %Cr + 1.73 %Si + 0.88 %Mo   (= 35.04)
- Ni_{eq} = %Ni + 24.55 %C + 21.75 %N + 0.4 %Cu   (= 14)
- Ferrite fraction (%) = -20.93 + 4.01 Cr_{eq} - 5.6 Ni_{eq} + 0.016T (where T°C is annealing temperature) **(= 41.18 + 0.016T = 58.0)**
- PREN = %Cr + 3.3 (%Mo = 0.5 %W) + 16%N
- **PREN = 54.4**
- **CPT = 76°C**

Cost: From Wikipedia values, for a kilogram of alloy, the cost of components is calculated to be 6.10GBP, and the price of a 50g ingot to be 0.31GBP.

Processing Steps

This is our plan for processing the alloy to maximise corrosion resistance and strength. We intend to make measurements of the hardness and phase fractions between key steps and so numerical values may be tweaked to optimise the results.

- Ingot casting:
  - Melt the iron, molybdenum and nickel in a crucible (2650°C)
  - Melt chromium in a separate crucible at a lower temperature (2000°C)
  - Reduce the temperature of the iron melt and mix in the chromium to the melt thoroughly (to prevent the chromium from boiling).
  - Zone levelling if possible.
  - Water quench to room temperature.
- Heat treatment 1:
  - Seal into a quartz ampule with an argon atmosphere to prevent unwanted byproduct formation.
  - Preheat using an induction coil to near 1000°C (where colour changes to orange-yellow) to heat quickly past temperatures where intermetallics form.
  - Transfer to furnace and anneal at 1050°C for 1 hour to balance duplex phase fractions [5].
  - Break ampule and water quench to avoid intermetallic formation.
- Cold working (contingent on analysis of mechanical properties):
  - Cold roll to 80% of original thickness to get a work hardening effect.
- Heat treatment 2:
  - Anneal at 475°C for 1 hour to initiate "α embrittlement" (spinodal decomposition of the ferrite) to increase strength via spinodal hardening at the expense of toughness.
  - Water quench.
- Surface passivation:
  - Polish all surfaces (to 2400 grit minimum) to mechanically remove high temperature oxide scale. Aim to create a smooth rounded surface with no crevices or sharp corners, because "active" corrosion surfaces can be induced by oxygen deprivation within tight crevices or pits [6].
  - Chemical passivation in low strength (0.5M) citric acid for 5 minutes to selectively remove ferrous oxides [6] and leave the surface Cr and Mo rich. (Or several hours in aerated deionised water to create a continuous hydrated Cr(III) film).
  - Thorough cleaning in deionised water and dry with hairdryer.
  - (If passivated in water: allow several spare days for Cr and Mo to replace the depleted region below the oxide layer before corrosion test).

Strengthening mechanisms targeted:
- Dual phase structure and Hall-Petch effect: the interfaces of grains of different phases act as barriers to dislocation motion. The alloy benefits from the higher intrinsic strength of ferrite and high work hardening rate of γ. The nucleation of γ along grain boundaries also refines the microstructure.
- Substitutional solute solution strengthening: The different atomic radii of the atoms create strain fields which increase the energy required for dislocations motion. The additions will be unevenly partitioned between the phases, with molybdenum in particular strengthening the ferrite phase.
- Spinodal hardening: the short anneal at 475º leads to a spinodal decomposition of ferrite into Cr-rich α' and Fe-rich α phases. Internal strain is induced by the coherency strain between the periodic phases, hindering dislocation motion. Dislocations are generated and accumulated at grain boundaries, increasing strength (more so than standard precipitate hardening) but reducing ductility. [9]
- Work hardening: cold rolling the alloy will increase the dislocation density and entanglement.
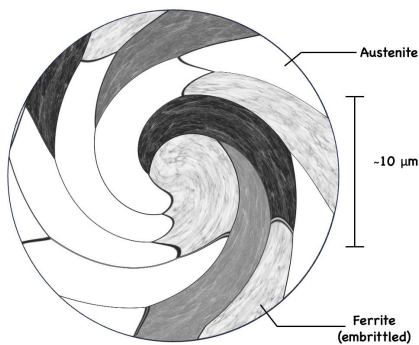
Microstructural considerations:

Figure 1: a schematic of the desired microstructure

To achieve the strengthening mechanisms above, we would want small grains of γ and ferrite, with the ferrite embrittled into an iron-rich ferrite and a chromium-rich ferrite.

We want to avoid deleterious TCP phases such as σ, χ, and μ from forming. This is because their formation can deplete the surrounding area of alloying additions [10,11] (reducing corrosion resistance), they form rod-like morphologies that could act as sharp point for crack propagation [11], and they would also reduce the amount of ferrite available for embrittlement if they are formed prior to that. μ forms in a narrow temperature range (e.g. around 650K [7]) but is rarely observed due to kinetics [10]. σ and χ, however, are frequently observed at higher temperatures (up to 1300K in some cases) [11]. We chose heat treatments such that we don't ever hold the alloy in these temperature ranges, and we always try to anneal and quench quickly through these temperature ranges, which often works in practice[11]. Additionally, the effect of χ forming from heating during the first anneal is lessened by the anneal itself, since χ dissolves at high temperatures readily [7]. Other TCP phases such as R, MoNi, and λ Laves, are observed in Fe-Cr-Mo-Ni alloys [8,12] but our composition should provide a thermodynamic barrier to formation [10].

Metal carbides with stoichiometry $M_{23}C_6$ can form from γ even at very low carbon concentrations (<0.03wt.%), which can transform into other stoichiometries upon cooling[8]. Our measures to prevent TCP intermetallic formation should also prevent metal carbide formation [8]. Bainites and martensites are unlikely to form based on the low carbon concentration and the stability of γ [1].

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