

62B.0 MAXIMIZING SCRAP RECYCLING BY DESIGNING COPPER TOLERANT STEEL COMPOSITIONS

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This project started in the Fall of 2021 and is supported by the Advanced Manufacturing Office of the Department of Energy. The research performed during this project will serve as the basis for the PhD thesis of Henry Geerlings.

62B.1 Project Overview and Industrial Relevance

The recycling of scrap in steel production is appealing from both an economic and ecological perspective. However, accumulation of residual elements such as copper, tin, and others in the steel scrap stream has grown with the increasing amount of integrated electronics in appliances, vehicles, and other equipment [62B.1]. While the supply of end-of-life steel is projected to triple by 2050 [62B.2], copper accumulation bottlenecks the amount of scrap that can be recycled without causing cracking during thermomechanical processing. With hand sorting and pig iron dilution being the current methods for copper dilution upstream of casting, this work aims to mitigate hot shortness downstream of solidification.

Most steels contain some amount of copper, often <0.1 wt.% for increased hardening and corrosion resistance [62B.3]. At high enough copper concentrations, however, steel surface oxidation during hot working can cause insoluble copper (and other residual elements) to be rejected and enriched at the steel-scale interface. If this enrichment exceeds solubility in austenite, it can form a liquid phase capable of penetrating subsurface austenitic grain boundaries and embrittling the material. This form of liquid metal embrittlement is called “hot shortness”, and leads to cracking of the material when forged in oxidizing atmospheres. The effects of hot shortness are readily observed on a workpiece surface, shown in Figure 62B.1.

While pig iron is currently employed to dilute the concentration of copper in scrap steel to acceptable levels, this energy intensive process often counteracts the economic and environmental benefits of recycling scrap to begin with [62B.4]. By elucidating the dependency of hot shortness on parameters such as oxidation rate, copper solubility, and microstructure, this work aims to increase the tolerance of copper in several steel products, thereby widening the applicability of recycled steel and minimizing the need for pig iron dilution. In turn, US steel producers could see significant energy and financial savings. This project targets four steel products that, from an industrial perspective, would benefit from increased scrap/copper tolerance: (1) low-carbon sheet, (2) low-carbon plate, (3) medium-carbon bar, and (4) high-carbon wire. With many of these products currently allowing for <0.1 wt. % copper, our metric of success is increasing copper tolerance to >0.15 wt. %.

This work is a collaboration between multiple CSM IUCRCs (CANFSA, ASPPRC), national labs, and several industry partners. With the goal of increasing copper tolerance in recycled steel scrap, our research efforts are divided into seven tasks, listed below with their relevant entities:

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|---|--------------|
| 1. Scrap supply chain analysis | (NREL) |
| 2. Melting in the electric arc furnace | (ASPPRC) |
| 3. Hot shortness casting and direct hot charging | (ASPPRC) |
| 4. Hot shortness during thermo-mechanical processing | (CANFSA) |
| 5. Materials characterization for subsequent steel processing | (CANFSA) |
| 6. Develop machine learning model for hot shortness data | (Mines) |
| 7. Techno-economic analysis | (NREL/Mines) |

While each of these tasks play a vital role in composing the overall project goal, this report specifically focuses on Tasks 4 and 5.

62B.2 Previous Work

62B.2.1 Literature and Research Approach

Mitigation of hot shortness in copper enriched steels has largely focused on (1) decreased oxidation rate, (2) increased copper solubility within austenite, and (3) increased occlusion of copper into the oxide. Each of these mechanisms ultimately share the goal of decreasing the formation of enriched liquid copper at the steel-oxide interface—known to back-diffuse into austenitic grain boundaries, causing them to crack under stress.

The addition of alloying elements can help hinder hot shortness by some combination of the mechanisms listed above. Nickel is perhaps the most well-known additive; providing both increased copper solubility in austenite, as well as promoting occlusion of copper-rich metal in the oxide. In copper/nickel ratios at or below 1, surface hot shortness is averted simply by avoiding the formation of copper rich liquid and instead promoting only solid γ iron during oxidation [62B.5]. However, due to its relatively high cost, the addition of nickel alone is not a feasible solution to hot shortness (i.e. it is likely cheaper to perform pig iron dilution). Silicon has also been observed to mitigate hot shortness in amounts of 0.1-0.2 wt.%. This is because it readily oxidizes at high temperature, impeding the transport of iron to the surface thus slowing the oxidation rate of the steel [62B.6]. Hot shortness may also be enhanced by the presence of other alloying/tramp elements. Tin, for example, actually *increases* the tendency of hot shortness in a manner almost completely opposite to nickel. This is due to a decreased solubility of copper in austenite as well as a lowered melting point of the copper enriched liquid [62B.6]. Trace amounts of tin in fact greatly increase the amount of nickel required to counteract its effects in preventing hot shortness. These competing interactions highlight why the mitigation of hot shortness through alloying additions must take into consideration all relevant elements and their complex interdependencies.

Conversely, processing parameters can also minimize the tendency for steel to undergo hot shortness. By using an inert gas atmosphere during hot working, oxidation (and consequently hot shortness), can be avoided. However, this solution does not scale efficiently to a production/forging scale. Austenitic microstructure can also play a part in affecting hot shortness, given that it is the matrix in which enriched liquid copper penetrates. Grain size and grain boundary distribution along the steel-oxide interface have been shown to affect the diffusion and wetting of enriched liquid copper into austenite [62B.7]

62B.2.2 Continued Work

Earlier work performed in 2003 by a previous CSM graduate student, Luis Garza, characterized the workability and hot shortness observed in 1045 steel at forging temperatures using the Gleeble thermomechanical testing device [62B.8]. Leftover bar material from that study has been repurposed for this project, fitting into one of the four steel products of interest, namely, medium-carbon bar.

62B.3 Recent Progress

Six bars of 1045 steel with diameters ranging from 1" – 1.688" were procured from previous work. Chemical analysis was performed on each, the results of which are shown in Figure 62B.2. It was found that two bars shared nominally identical chemistry, and that copper contents ranged from 0.21 - 0.38 wt. % among the bars; additional chemistry results are shown in Table 62B.3.

Remaining barstock material has been machined in-house to prepare Gleeble compression cylinders. Actual Gleeble experiments are still being developed in order to establish a standard thermomechanical process route representative of typical steel forging. Similar to the thermal/load profile used on this material in previous work, we aim to establish a baseline dataset for hot shortness observed during thermomechanical processing (Task 4) in terms of oxidation time/temperature, deformation condition, and atmosphere. It is of interest to derive a metric for describing the extent of hot shortness for use in a predictive model that can synthesize scrap chemistry, processing, and hot shortness in a quantified manner (Task 6). Sections of each unique bar chemistry have been submitted for machining in order to perform dilatometry measurements. For each copper amount, dilatometry experiments with cooling rates of 100, 10, 1, 0.1, 0.01 °C/s will be performed to generate continuous cooling transformation diagrams. These in turn will inform how tramp element amounts (copper, tin, nickel, etc.) affect the onset of phase transformations as a function of cooling

rates representative of those performed on steel products (Task 5). A knowledge of how tramp element concentrations influence phase transformations is crucial for controlling mechanical properties in structural steel products.

62B.4 Plans for Next Reporting Period

With this project being in its first year, most work has been focused on material procurement and characterization. In the coming months, some of the immediate next steps for this work are:

- Procurement and characterization of material representing the other 3 steel products of interest.
- Dilatometry experiments of the medium carbon barstock once machining is complete.
- Higher volume of data from the Gleeble thermomechanical system to establish a training dataset.
- Drafting of a review paper focused on hot shortness observed during thermomechanical processing.

62B.5 References

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- [62B.8] L.G. Garza, C.J. Van Tyne. Surface hot-shortness of 1045 forging steel with residual copper, *Journal of Materials Processing Technology*. 159 (2005) 169-180.

62B.6 Figures and Tables

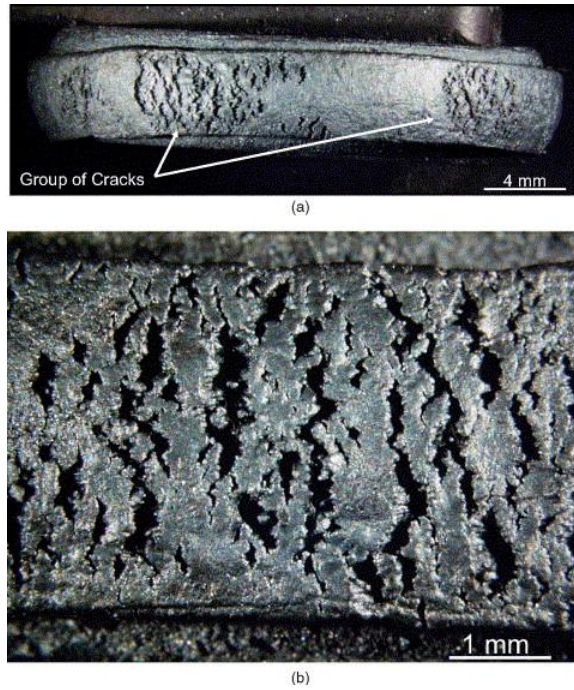


Figure 62B.1 Optical imaging of hot shortness cracks observed in a flanged compression specimen of 1045 steel with 0.35% copper. Specimen was oxidized for 10 minutes at 1160 °C before being compressed in a Gleeble, causing hot shortness shown in (a) groups along the circumference of the cylinder, and (b) close-up into one of the crack groups [62B.4].

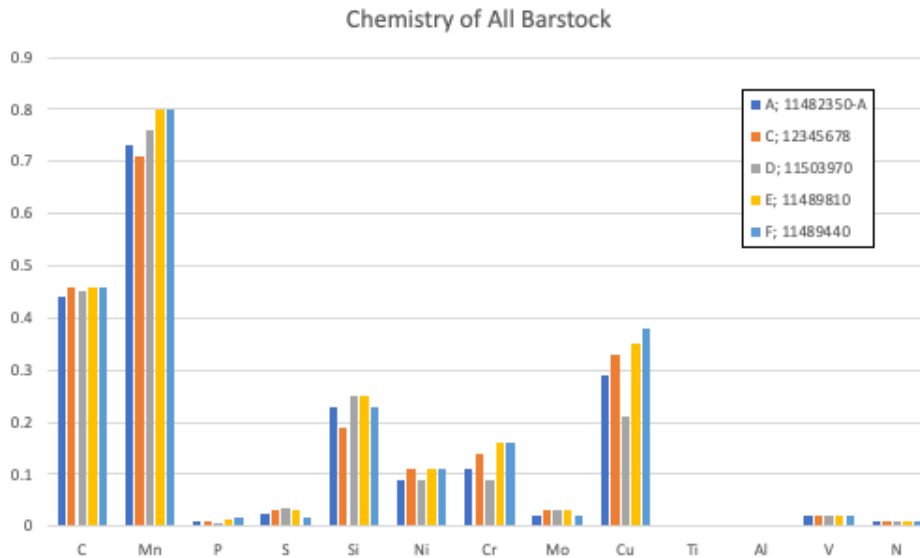


Figure 62B.2 Measured chemistry profiles for the five unique bar chemistries procured from previous studies of L. Garza and C. Van Tyne. The sixth bar (B) has been removed as it shared identical chemistry to bar A. While nickel concentration is relatively constant, copper contents range from 0.21 – 0.38 wt. % copper.

Table 62B.3 Complete chemical makeup (in wt. %) of the five unique bar chemistries shown in Figure 62B.2.

| | Bar A | Bar C | Bar D | Bar E | Bar F |
|----|---------|---------|---------|---------|---------|
| C | 0.44 | 0.46 | 0.45 | 0.46 | 0.46 |
| Mn | 0.73 | 0.71 | 0.76 | 0.8 | 0.8 |
| P | 0.01 | 0.01 | 0.007 | 0.015 | 0.016 |
| S | 0.024 | 0.031 | 0.037 | 0.032 | 0.017 |
| Si | 0.23 | 0.19 | 0.25 | 0.25 | 0.23 |
| Ni | 0.09 | 0.11 | 0.09 | 0.11 | 0.11 |
| Cr | 0.11 | 0.14 | 0.09 | 0.16 | 0.16 |
| Mo | 0.02 | 0.03 | 0.03 | 0.03 | 0.02 |
| Cu | 0.29 | 0.33 | 0.21 | 0.35 | 0.38 |
| Ti | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Al | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| V | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| N | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Fe | Balance | Balance | Balance | Balance | Balance |