

The effect of scrap originating trace elements on the properties of low alloyed steels

Shahroz Ahmed^{1*}, Ali Sabr¹, Ari Peltola², Olli Oja², Sanna Järn², Antti Kaijalainen³, David Penney⁴, Pasi Peura¹

¹ Metals Technology Research Group, Tampere University, Tampere, Finland

² Product Development, SSAB Europe Oy, Hämeenlinna, Finland

³ Materials and Mechanical Engineering, Oulu University, Oulu, Finland

⁴ Metals Coating Group, Swansea University, Swansea, Wales, United Kingdom

E-mail: shahroz.ahmed@tuni.fi

Abstract. The present intention to reach fossil-free steel manufacturing will inevitably result in an increase in the use of steel scrap as a raw material for steel production. Consequently, the amounts of elements, seen as impurities, will increase in steels. This has already been seen in electric arc furnace (EAF) processed steels, where the Cu and Sn levels have doubled in some cases after 1980's. This may cause problems, as it is well-known, that some impurity elements have harmful effects on the properties of steel. This has been widely studied in low-alloy steels containing chromium and molybdenum which are widely used in components for the petroleum and electrical power generation applications. However, limited number of studies have been performed on formable steel grades, and the published reports/articles have mostly concentrated on the effects of P and B. Thus, there is still a need to understand the roles of other impurity elements. In the present study, a formable C-Mn steels containing additions (either individually or in combination) of Cu and Sn is investigated. The samples were cold rolled and annealed following typical time-temperature profiles of modern continuous annealing lines. Mechanical and forming properties (incl. bending and cupping tests) are determined as well as elemental profile analysis is conducted. The results identify that minor additions of impurity elements, in this case Cu and Sn, does not affect the mechanical and forming properties of low alloyed formable steel grades considerably.

1. Introduction

In order to reduce the carbon footprint from steel making, there is a great interest in transforming to 'Fossil Free Steels'. The term 'Fossil Free Steels' refers to producing steels by utilizing renewable sources of energy i.e., in practice using direct reduction with hydrogen and Electric Arc Furnace (EAF) route instead of blast furnace. Steel making through EAF requires increased use of scrap as a raw material, and as a result of this requirement the amount of trace or tramp elements, such as P, As, Cu, Sn etc, in steels will be increasing over the time. These trace or tramp elements can segregate to grain boundaries and may effect the mechanical, forming and coating properties [1], [2]; however, in some



cases it has been reported that some elements alone or in combination may have positive impact on properties [3].

Prior studies conducted on the topic of 'segregation of trace elements' identify the conditions for segregation of solute atoms, for example, Seah [4] studied grain boundary segregation and presented the relationship of atomic size and enthalpy of trace elements in Fe. He reported that elements with large atomic size have a higher tendency to segregate on grain boundaries and the driving force for segregation is related with elastic mismatch energy of solute and solvent atoms, and the differences in atomic dimensions. Gibson et al. [5] presented an elemental map by studying the ratio of 'solute/solvent surface energy (γ)' and 'non-dimensionalized heat of mixing ($\Delta H^{\text{mix}}/RT$)'. They also showed that the tendency of embrittlement, solute enrichment and potential increase in cohesion can be predicted by calculating the surface energy and heat of mixing at equilibrium temperature.

The effect of different trace elements, such as P, As, Sb, Sn etc., on the mechanical and forming properties have been previously investigated. For example, Rege et al. [6] studied the behaviour of P in Ti and Ti+Nb stabilized high strength IF steel during different stages of thermomechanical processing. They reported that P starts to segregate during coiling and the amount of segregation was reduced in the case of Nb alloying. They also added that cold work embrittlement resistance improved when P content was lowered from 0.06 to 0.014. Pilkington et al. [7] conducted creep and charpy impact tests to investigate the effect of P, As, Sb, Sn on the creep and impact strength of heat treated Cr-Mo steel. They reported that each element behaves differently under different testing conditions. It was found from their study that As do not segregate to grain boundaries while Sb and Sn show segregation.

Copper and tin are trace elements difficult to remove from steel. Copper is also one of the alloying elements which increase strength, hardenability and improves corrosion resistance but it should be kept to 0.2% to avoid hot shortness [1]. The effect of increasing Cu content, from 0.02 to 0.8%, was studied by Houpert et al. [8] during different stages of thermomechanical treatments and they showed that hot shortness began to appear in the steel containing more than 0.15% Cu. Study by Imai et al. [9] showed that cracking due to hot shortness occurred in mild steels during high temperature deformation; they also showed that adding Ni to mild steels can reduce hot shortness to a certain extent. Yamada et al. [10] investigated extra low carbon steel with different Cu contents and reheating temperatures. Increasing Cu was reported to increase tensile strength by solid solution strengthening and decrease elongation and anisotropy parameter.

Sn is common trace element and its content is generally below 0.03 % because Sn can segregate to grain boundaries and cause hot shortness, temper embrittlement and decrease forming characteristics [1]. Stephenson [11] reported that increasing Sn content in steels will result in rise of ductile brittle transition temperature and reduction in shelf energy. Bruscato [12] showed that increasing Sn content in Cr-Mo steels, increases the susceptibility to temper embrittlement. Peng et al. [13] studied the effect of Sn (0.004-0.045%) on hot ductility of 20CrMnTi steel (0.02 Cu). They reported that samples with less than 0.045% Sn, show no Sn-rich phase at scale/steel interface and concluded that the reduction in hot ductility caused by Sn segregation at austenite grain boundaries reduced the cohesion of grains combined with the formation of thin ferrite film on austenite grain boundaries.

There are limited studies conducted on steels that shows the combined and individual effect of Cu and Sn on the forming and coating properties, specially in low alloyed steels. Sato et al. [14] predicted that the content of Cu and Sn in steels produced by EAF will increase in the future, as shown in Figure 1. The data from Figure 1 indicates that, thorough studies are required on steels grades that contain more than 0.2% Cu and 0.025% Sn, in order to produce fossil free steels for future applications.

In this study, the individual and combined effect of 0.3% Cu and 0.03% Sn on the properties of low alloyed steel is investigated; this work mainly concentrates on continuously annealed steels and does not consider the effects of trace elements during hot deformation. The results from this work would indicate the possibility of using low alloyed steel grades with higher content of trace elements for future applications, specially in the forming industry.

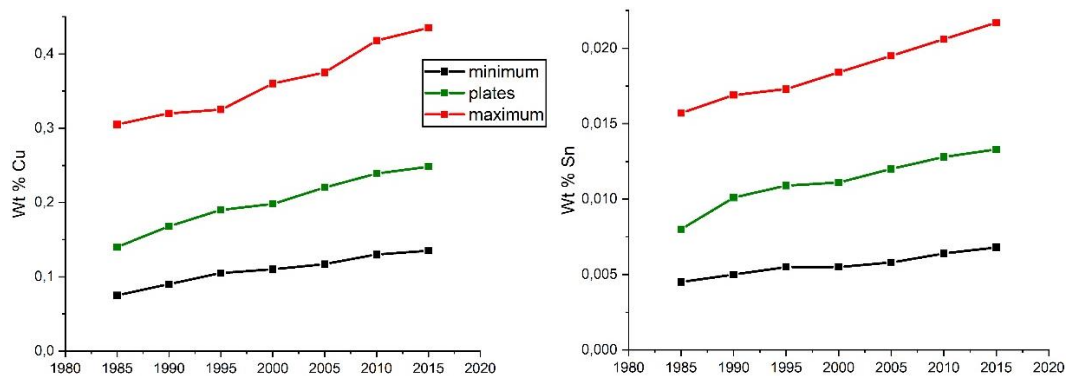


Figure 1: Increment in the content of Cu and Sn in steels over the years (predicted by Sato et al. [14]), Figure modified from [14].

2. Methods and Materials

The aim of this work was to investigate the individual and combined effect of Cu and Sn on the properties of low carbon steels. In order to study the effect of Cu-Sn on steels; four low carbon-manganese steels containing Cu-Sn were designed, the chemical composition of the steels is given in Table 1. From Table 1, it can be seen that each steel is distinct from the other; steel 1 contains no traces of Cu and Sn, steel 2 contains Cu but no Sn, steel 3 contains only Sn and steel 4 contains both Cu and Sn. The steel melts were first vacuum casted as slabs, then the slabs were subjected to hot rolling followed by cold rolling to thickness 0.8 mm. Micrographs (not shown here) from optical microscopy indicated that there are differences in the grain sizes after hot rolling. The grain size data in ASTM are 11.3, 12.3, 10.6 and 12.4 for steel 1, steel 2, steel 3 and steel 4 respectively.

Table 1: Chemical composition of the investigated steels.

Steel type	Elemental composition in wt.%		
	C	Cu	Sn
Steel 1	0.05	-	-
Steel 2	0.05	0.3	-
Steel 3	0.05	-	0.03
Steel 4	0.05	0.3	0.03

2.1. Annealing treatment with Hot Dip Galvanizing Simulator and Gleeble

The cold rolled 0.8 mm thin steels were cut into 125 × 210 mm rectangular sheets for annealing. The annealing cycles were conducted in a Hot Dip Galvanizing Simulator (HDS) without dipping to molten zinc; Figure 2 shows the annealing cycle, conducted in HDS. Gleeble 3800[®] thermomechanical simulator was also used to conduct the annealing cycle for one rectangular sheet from each steel.

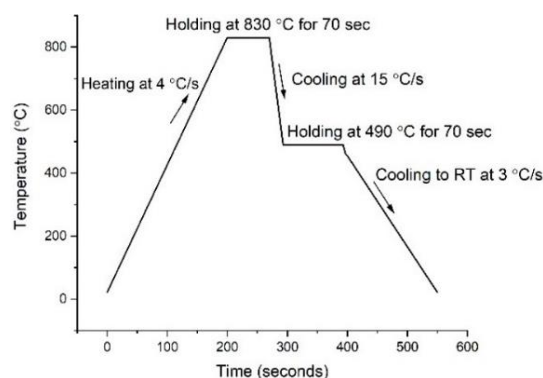


Figure 2: Heat treatment cycle for the steel samples 1 – 4 conducted in HDS and Gleeble.

2.2. GDOES measurements

A GDA750 glow discharge optical emission spectroscope Spectruma Analytik GmbH GDOES analyser was used to measure elemental depth profiles from surface of annealed samples down to 35 μm . The measurements were performed in a high sputter rate mode using constant current (20mA/700V).

2.3. Mechanical and Forming tests

After annealing cycles, the samples were investigated for their mechanical and forming properties by using uniaxial tensile tests, three point bending tests and Erichsen cupping tests.

2.3.1. Uniaxial tensile tests. The tensile tests were conducted with Instron 8800 uniaxial servo hydraulic materials testing machine. Tensile specimens with a gauge length of 25 mm and a gauge width of 9.5 mm were prepared from the annealed sheets. The tensile test was conducted according to the standard E8/E8M-22; the strain rate in the tests was $1 \times 10^{-3} \text{ s}^{-1}$ and the direction of loading was transverse to the direction of rolling. The strain was calculated by using a LaVision SMC 5M-140 optical extensometer with Davis software for Digital Image Correlation (DIC).

2.3.2. Three point bending tests. The three point bending tests were conducted to study the formability on samples that were annealed in Gleeble. After annealing, the specimens were cut to standard dimensions of 50 x 50 mm to conduct the tests. The test was performed using a universal testing machine with a low-friction roller carrier and a 0.2 mm radius punch, connected to a servo-hydraulic materials testing machine (specifically Instron 8800) in accordance with the specifications of standard VDA 100-238. The sample was loaded in the transverse direction of rolling at a predetermined punching speed of 20 mm/min until failure occurred. The bending angle at maximum force F_{max} , referred to as α° , was determined using equation 1 (taken from VDA 100-238 standard), the equation considers the test setup and the force-displacement data.

$$\alpha^\circ = 2 \times \left(-\text{Arctan} \left(\frac{\sqrt{\left((R+a)^2 - \left(\frac{-\sqrt{(h^2-4g \cdot i-h)}}{2g} \right) + \left(R + \frac{L}{2} \right) \right)^2 - (R+a-s)}}{-h - \frac{\sqrt{h^2-4g \cdot i}}{2g}} \right)} \right) \times \frac{180}{\pi} \quad 1$$

where g , h , and i are test parameters defined depending on roll diameter (R), sample thickness (a), the distance between rollers (L), and displacement value (S) corresponding to maximum force.

2.3.3. Erichsen cupping tests. Erichsen cupping tests were performed with Erichsen 142-40 machine and according to the standard SFS-EN ISO 20482 standard.

3. Results and Discussions

3.1. GDOES

The results from GDOES are given in Figures 3 (a-d). For the minor elements (<1 wt.%), the accuracy of GDOES is low and typically within ± 5 -20%. From Figures 3 b and d, it can be seen that copper content is fairly the same throughout the depth of the specimen which means that there is no enrichment of Cu in the near surface region. GDOES has its limitations for the detection of minor elements and that is why the Sn data shown in Figures 3 should be considered with caution. Determining absolute Sn content needs more studies.

For reliable data about the segregation of elements to outermost surface and grain boundaries, Auger electron spectroscopy (AES) or atom probe tomography (APT) studies are required.

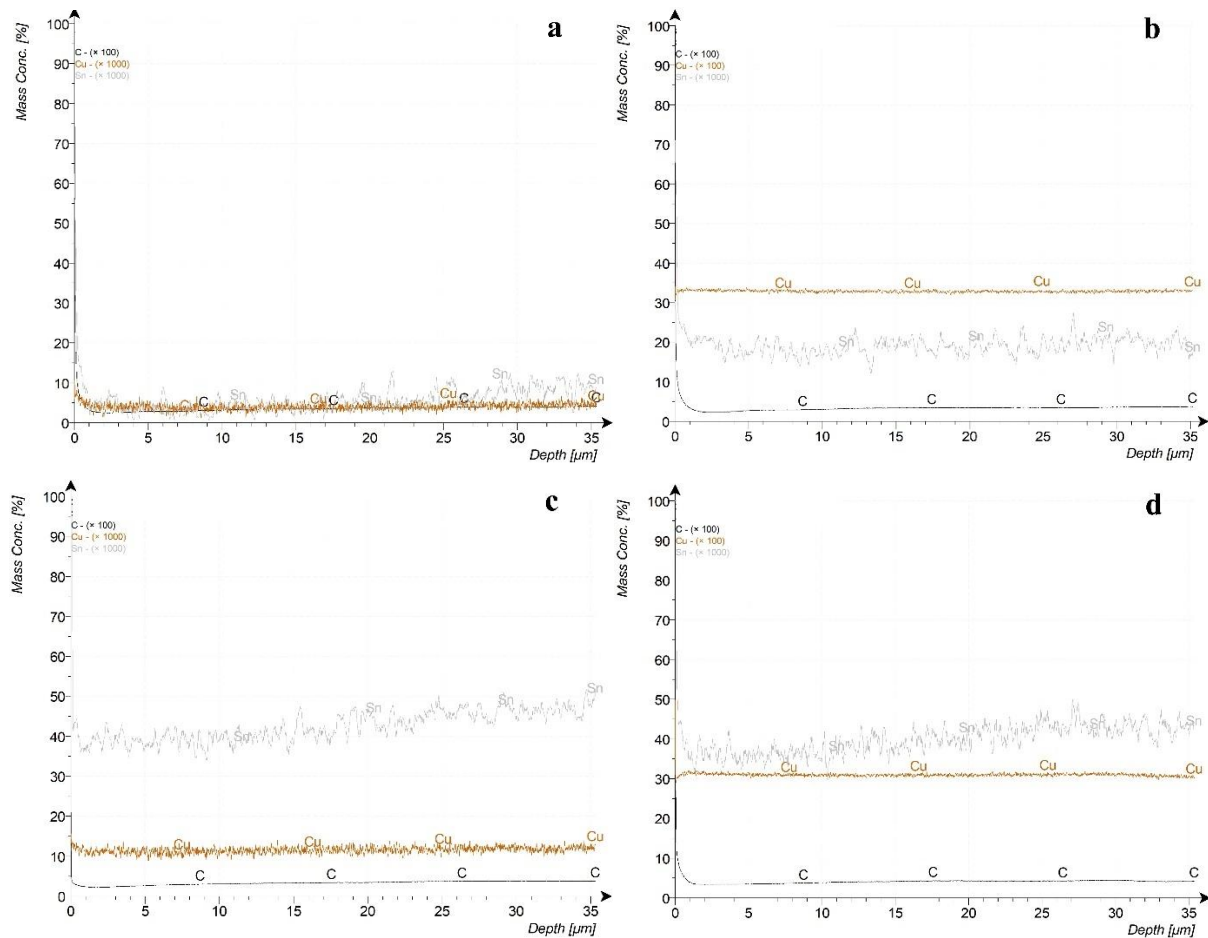


Figure 3: GDOES results from annealed steel samples (a) steel 1, (b) steel 2, (c) steel 3, (d) steel 4. Note different enhancement factors for Cu.

3.2. Tensile tests

The stress-strain data obtained from uniaxial tension tests are shown in Figures 4 (a and b) and the mechanical properties of samples are presented in Table 2. The samples were not subjected to skin pass rolling that is why the upper and lower yield points and yield point elongation are visible in Figure 4a. From the stress-strain curves (Figure 4a) it can be seen that minor additions of alloying in steel 2 and 3 suppressed the elongation slightly but the strength levels were almost the same in all of the samples. The total and uniform elongation of steel 4 (shown from stress-strain curve in Figure 4a and Table 2) are almost the same as steel 1, which might mean that minor additions of Cu and Sn together can be beneficial for low alloy steels but the combined effect of both Cu-Sn on the mechanical properties on low alloy steels needs more investigation. From Figure 4b, it can be seen that instantaneous strain hardening exponent curves looks similar for each steel and there are no major differences.

From the mechanical tests, it was seen that individual alloying of Cu and Sn (steel 2 and 3) slightly reduced the elongation but the combination of Cu-Sn alloyed steel (steel 4) had almost the same elongation. There were indications (Figure 4 a and b) that Cu alloyed steel had slightly higher strength.

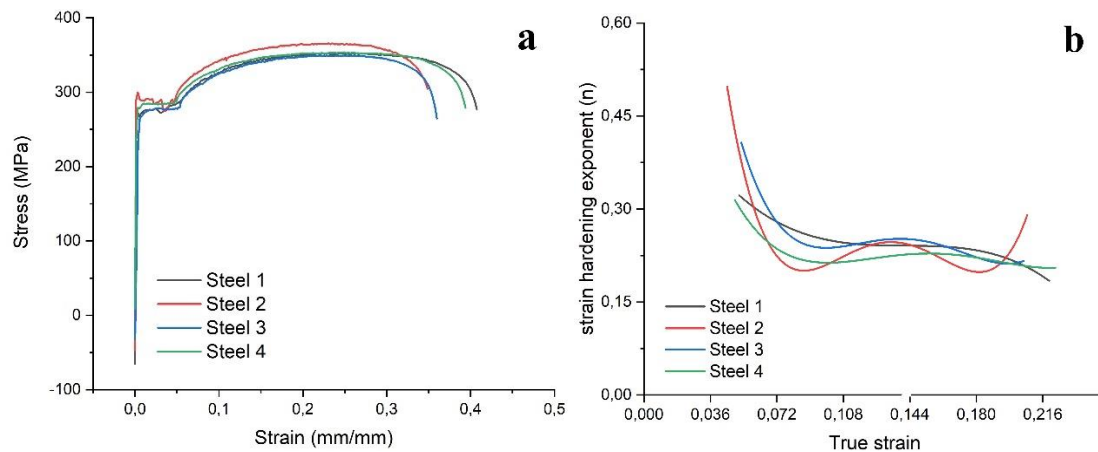


Figure 4: (a) stress-strain curves of samples 1 - 4 obtained from tensile tests (b) work hardening rate values plotted against true strain.

Table 2: Mechanical properties of samples.

Steel type	Upper yield point (MPa)	Lower yield point (MPa)	Uniform elongation (%)	UTS (MPa)	Total elongation (%)	Average n value for 10-20 % elongation
Steel 1	277	270	24.7	352	40.7	0.24
Steel 2	289	273	23.0	365	34.9	0.22
Steel 3	278	276	22.8	349	36.0	0.23
Steel 4	284	282	24.9	353	39.3	0.22

3.3. Three point bending tests

The bendability of steel samples using three-point bending tests (VDA 100-238) after annealing in a Gleeble simulator following the annealing cycle. The α° values from all four steel samples are presented in Table 3 and Figure 5 shows force vs displacement curves. The obtained α° values indicated high formability for all the steels. However, the inclusion of Cu and Sn in the steel compositions reduced the bendability to a slight degree as compared to the steel with no alloying. Steel 1, without any trace elements, had a bending angle of 115.6 degrees, while Steel 2, containing Cu, exhibited a slight decrease of 3 degrees. Steel 3, alloyed with Sn, had comparable bendability to steel 1, but Cu and Sn alloyed steel had slight lower bending angles than Steels 1, 2, and 3. The lowest bending angle achieved in three point bending test was from Cu-Sn alloyed steel but the difference in the bending angle was small.

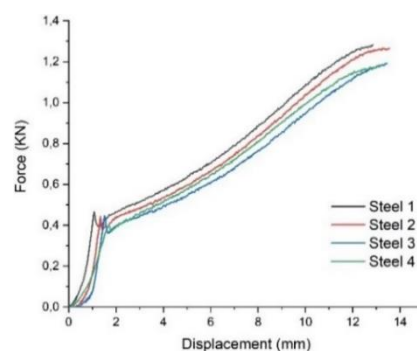


Figure 5: Force displacement curves from three point bending tests.

The bending test results show that minor additions of Cu and Sn in low alloy grades does not significantly affect the forming and mechanical properties of low alloyed grades.

Table 3: α° values obtained from bending tests.

Sample	Displacement (mm)	Force (kN)	α° (α Fmax) (degrees)
Steel 1	12.84	1.28	115.6
Steel 2	13.54	1.27	112.7
Steel 3	13.45	1.19	115.5
Steel 4	13.16	1.18	105.5

3.4. Erichsen cupping tests

The forming results from Erichsen tests are presented in Table 4. These results indicate that the change in elemental composition on low alloy formable grades had minimal changes in the cupping tests.

Table 4: Results from Erichsen cupping tests.

Sample	Thickness (mm)	Drawing speed (mm/min)	Holding force (kN)	Cup height (mm)
Steel 1	0.8	10	10	11.1
Steel 2	0.8	10	10	11.1
Steel 3	0.8	10	10	11.0
Steel 4	0.8	10	10	11.1

4. Conclusion

The individual and combined effect of addition of Cu and Sn on the forming properties of low carbon formable grades were investigated. The results suggest that there are negligible changes in the forming characteristics when Cu and Sn is alloyed with these grades. There were some indications that the combined effect of Cu and Sn might be favourable but this phenomenon needs more investigation. From this investigation, it can be concluded that minor additions of Cu and Sn does not affect the forming properties to a large extent.

Acknowledgement

The authors would like to acknowledge the efforts of Juha Uusitalo from Oulu University for conducting Gleeble treatments. The authors would also like to acknowledge Kyle Carter and Dan Britton from Swansea University for their work with Hot Dip Galvanizing Simulator. The authors are also grateful to Business Finland for funding the project ‘Fossil Free Steel Applications’.

References

- [1] Leroy V, Defourny J, and D'Haeyer R 1995 *Effects of tramp elements in flat and long products*
- [2] Xu S, Brown J R and Tyson W R 2006 *Steel Res. Int.* **77** 825–835,
- [3] Rod O, Becker C and Nysten M 2006 *Jernkontorets Fornkning* IM-2006-124
- [4] Seah M P 1980 *Acta Metall.* **28** 955–962
- [5] Gibson M A and Schuh C A 2015 *Acta Mater.* **95** 145–155
- [6] Rege S J, Hua M, Garcia C I and Deardo A J 2000 *ISIJ Int.* **40** 191–199
- [7] Pilkington R, Dicken R, Peura P, Lorimer G W, Allen G C, Holt M and Younes C M 1996 *MSEA* **212** 191-205
- [8] Houpert C, Lanteri V, Jolive J M, Guttman, Birat M, Jallon J P and Confente M **1996** 32nd *conference of energy conservation USA*
- [9] Norio I, Nozomi and Kazutoshi K 1997, *ISIJ Int.* **37** 224–231
- [10] Yamada T, Oda M, and Akisue O 1995, *ISIJ Int.* **35** 1422–1429
- [11] Stephenson E T 1980 *Metall. Trans. A.* **11** 517–524
- [12] Bruscatto R 2013 *Conference proceeding of AWS annual meeting Cleveland*
- [13] Peng H, Chen W, Chen L and Guo D 2014 *High Temp. Mater. Process* **33** 179–185
- [14] Sato S, Takeuchi M, Mizukami Y, and Birat J P 1996, *Rev. Métallurgie* **93** 473–483