JERNKONTORETS
FORSKNING

D 819
(IM-2006-124)

Opportunities and dangers of using residual elements in steels: a literature survey

Report by Olivier Rod, Christian Becker, Margareta Nylén, KIMAB

Keywords:
Steel scrap, recirculation, residual elements, micro alloying, properties, iron and steel industry

Report JK 88042 2006-12-07
(ISSN 0280-249X)

Abstract

The growing recirculation of steel scrap coming mainly from the collection of obsolete products may result in a substantial increase of residual elements in steel, which is often considered as a problem. However, residual elements in scrap are used as effective micro alloying elements if the appropriate production is used.
The current restrictions on levels of residual elements have often been set from a cautious viewpoint. With a deeper understanding of the dynamics behind the interactions of different elements, it is reasonable to believe that the level of residual elements can be increased in some high quality steel products.

This study is aimed to give an overview of the situation and state of the art concerning residual elements in low alloy low carbon steels, their effect on processing and final properties of the steels and the way they are used today.

An overview of the possible effects of residuals elements on down-stream process and end properties of steels, classified by their nature in the steel, is proposed through a summarising figure.

The most remarkable trend in the literature is the dominance of Cu in the elements studied: most of the studies are concerned by the influence of copper, alone or in combination with other elements.

The effect of residual elements is presented in respect to their effect on:
Hot working: mainly hot-shortness problem related to Cu are studied, but even grain boundary segregation mainly of Sn.
Cold working: study of elongation and drawability. Residual elements mainly contribute to harden the matrix (Ni, Cr, Cu, Mo, Sn and As). Copper was shown in some cases to have positive effects on formability when processing and heat-treating the material properly.
Hardenability: most residual elements increase the hardenability by slowing down the ferrite and pearlite reactions.
End properties: most residual elements increase the strength and decrease the ductility, which is mainly due to solid solution hardening and also to precipitation.
Grain boundary embrittlement, is due to the segregation of elements at the grain boundaries during cooling, coiling and final annealing (mostly Sn, Sb, As, P).
Welding: most of the residual elements contribute to the hardenability in the HAZ in a more or less negative way.

Table of Contents

1. Introduction

The aim of this literature survey, together with feedback from the Swedish steel industry, is to give a basis for further investigations about residual elements in steel.
It is aimed to give an overview of the situation and state of the art concerning residual elements in steels, their effect on processing and final properties of the steels and the way they are used today. Focus is put on low alloy low carbon steels. Stainless steels are not considered.

2. Searching motor

Search was done using mainly CSA Metadex database, and even Weldresearch, IIW, and CORDIS (database about EU projects).
Search criteria shown in Table 1 have been used.

Table 1 Search criteria used. The red crosses indicate the search combinations that were studied. The red lines show the combination for which no reference was found.

	Residual elements	Tramp elements	Copper	Nickel	Tin	Vanadium	Manganese
Corrosion	X	X	▨	▨	▨	▨	▨
Formability	X	X	X	▨	X	------	------
Hardenability	X	X	X	▨	X	X	X
Strength	X	X	1990->	▨	▨	▨	▨
Ductility	X	X	------	▨	X	X	X
steel	X	X	▨	▨	▨	▨	▨
Weldability	X	X	X	X	X	▨	▨
Machinability	X	X	X	X	X	▨	▨

3. Recycling of steel – general facts

Steel is one of the more recycled materials. Iron and steel industry in Sweden is in a great extent based on scrap use. [1] The growing recirculation of scrap coming mainly from the collection of obsolete products may result in a substantial increase of tramp elements in steel. [2].
Scrap is not a waste material but a valuable raw material with a high energy content. Every ton of recycled steel scrap saves 1134 kg iron ore, 635 kg coal and 54 kg lime. The production of new steel from scrap in EAF (electric arc furnace) consumes about half of the energy necessary for producing steel from iron ore. Production of steel from scrap compared to the production based on reduction of iron ore with coke reduces the emission of CO2 and other harmfull gases and consumes less water too. Scrap purification has also economical aspects regarding the value of residual elements in steel.

Long products are manufactures usually with EAF route, while BOF (basic oxygen furnace) plants mainly produce flat products. Steel scrap makes for almost 100% of the iron-bearing charge in EAF steelmaking, while basic oxygen furnaces can process only up to 20% scrap. Europe and North America are increasing the skare of EAC steelmaking at the expense of integrated steel production and the trend appears to be long term. The driving forces for this change are strong: availability of scrap, social pressure to recycle materials and economic benefits to be reaped from the small structure associated with this short and slim production route. [3]

According to [4], the residual elements problem do not surface as long as steel scrap is used for making shapes, bars and other steel products that have lenient residual elements restrictions. Such a situation has been maintained until the obsolete accounted for 30% or less of all ferrous raw materials.

In Japan the generation of obsolete is predicted to exceed 40% of total steel production in 2010. In that case the steel scrap generation will surpass the demand unless steel scrap is used to make steel products other than shapes and bars, for example sheets. Composition of various steel grades available on the Japanese market is given in Table 2.

Table 2 Examples of composition of various grades of scrap on Japanese market.

Grade		Cu	Sn	Cr	Ni	Pb	Zn
heavy	HS	0.13	0.012	0.05	0.08	–	–
	H1	0.09	0.003	0.07	–	–	–
	H2	0.24	0.018	0.10	0.10	–	–
	H3	0.33	0.015	0.19	–	–	–
pressed	A pressed	0.64	–	0.03	0.11	–	–
	C pressed	0.64	0.40	0.05	0.06	–	–
	new punched	0.04	–	0.04	0.02	–	–
shredded		0.23	0.01	0.28	0.07	0.026	0.22
turnings		0.19	–	0.27	0.09	–	–

The most spread way of thinking is that the problem to be solved is the economic removal treatment of residual tramp elements in the steelmaking process. [5]

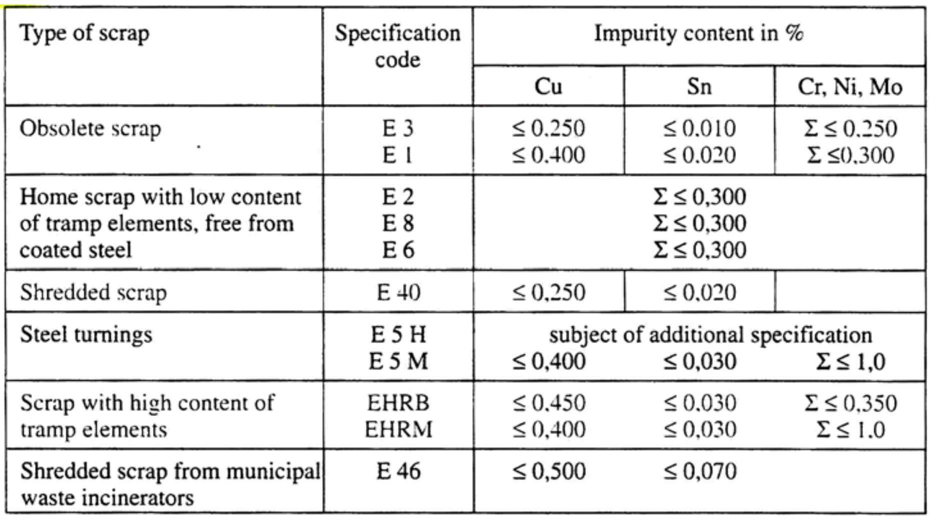
Copper and tin are the residual elements that adversely affect the hot workability of steel. According to some authors, in order to prevent the occurrence and accumulation of unrecyclable scrap, new technologies ensuring removal ratios of 55% for copper and 30% for tin have to be developed by 2010. [6]

Steel scrap is divided into home scrap, process scrap and obsolete scrap.

Since home and prompt scrap quantities are limited, an increase in scrap demand obviously leads to the following dilema. On one hand, the EAF intends to conquer new, higher quality steel markets, but on the other hand, it has to rely more on obsolete scrap, the quality of which decreases. [7]

In 1996, of a new Scrap Grading System (SGS) based on a clear description of scrap quality was introduced in Europe (Table 3). Quality has 2 components: scrap purity expressed in terms of metal (or iron) content and of level in tramp elements and scrap size and density [8]. This grading system is referred to in the Swedish system, where the scrap is even divided in different classes depending on the shape, size, state and origin (see reference [9]).

Table 3 European scrap grading system.



Type of scrap	Specification code	Impurity content in %		
		Cu	Sn	Cr, Ni, Mo
Obsolete scrap	E 3 E 1	≤ 0.250 ≤ 0.400	≤ 0.010 ≤ 0.020	Σ ≤ 0.250 Σ ≤0.300
Home scrap with low content of tramp elements, free from coated steel	E 2 E 8 E 6	Σ ≤ 0,300 Σ ≤ 0,300 Σ ≤ 0,300		
Shredded scrap	E 40	≤ 0,250	≤ 0.020	
Steel turnings	E 5 H E 5 M	subject of additional specification ≤ 0,400	≤ 0,030	Σ ≤ 1,0
Scrap with high content of tramp elements	EHRB EHRM	≤ 0.450 ≤ 0,400	≤ 0.030 ≤ 0.030	Σ ≤ 0.350 Σ ≤ 1.0
Shredded scrap from municipal waste incinerators	E 46	≤ 0,500	≤ 0,070	

4. Residual elements

An element can be regarded either as an alloying element or as a tramp element depending on its content in steel and on the steel grade being produced.

Residual elements in steel are usually defined as those elements left in the steel after refining which are not specifically required and in many cases are considered harmful to the product properties when present in a too high concentration. The most important residual elements are: Cu, Sn, Zn, Pb, Bi, Sb, As, Ni, Cr, Mo and V. [10]

There are 3 main mode of existence of residual elements in scrap: in pure state, as coating material and as alloying additions.[6]

Some metallurgical phenomena related to an increase in the level of tramp elements are clearly unfavorable, but some may be beneficial, depending on the final application of the product.[3]

In the following chapters, the modes of existence and effects of residual elements on processing and final properties of steels are treated, in a general matter and also through some more specified relevant case studies.

Tables in chapter 7 are summarising the results presented in some general studies on the influence of residual elements.

4.1 Sources of residual elements

Reference [6] lists sources of the main tramp elements in steel scrap:

The main sources of Cu are discarded passenger cars, structural steel with up to 0.5%Cu (mild resistance to corrosion and precipitation hardening), sheet.

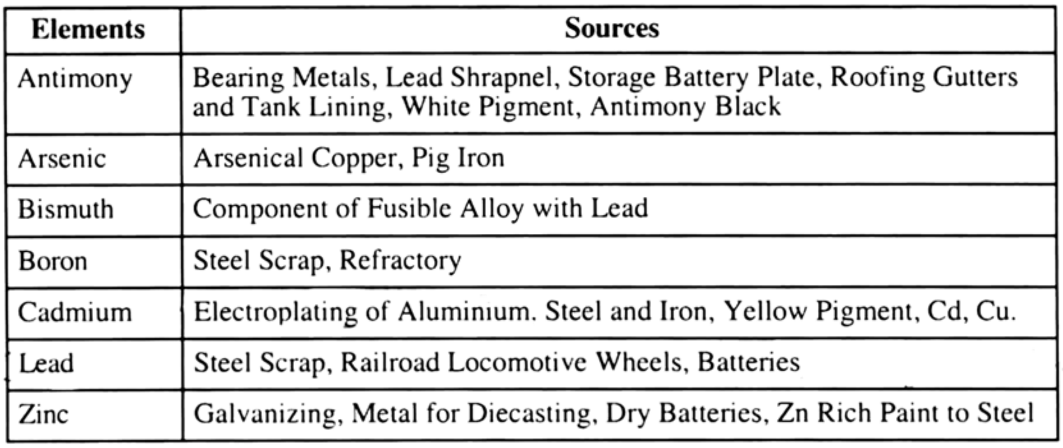
The main sources of Sn are post-consumer tinplate packaging and solders.

The main sources of Zn is protective coating.

The main sources of Pb (decreasing) are free-machining steels, solders and pigment in some paints.
Cr, Ni, Mo and V are used as alloying elements in numerous steel grades. Ni is moreover used as a constituant of the ZnNi coating of galvanised steel sheets.

This list is completed by Table 4, where the source of residual elements not usually monitored in steel making is given.

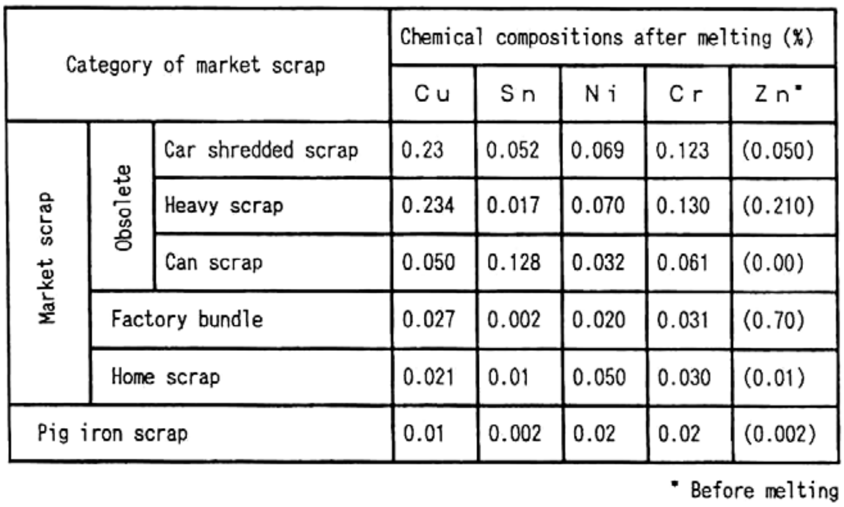
Table 4 Sources of tramp elements not usually monitored in steel making [57]



Elements	**Sources**
Antimony	Bearing Metals, Lead Shrapnel, Storage Battery Plate, Roofing Gutters and Tank Lining, White Pigment, Antimony Black
Arsenic	Arsenical Copper, Pig Iron
Bismuth	Component of Fusible Alloy with Lead
Boron	Steel Scrap, Refractory
Cadmium	Electroplating of Aluminium. Steel and Iron, Yellow Pigment, Cd, Cu.
Lead	Steel Scrap, Railroad Locomotive Wheels, Batteries
Zinc	Galvanizing, Metal for Diecasting, Dry Batteries, Zn Rich Paint to Steel

Table 5 presents a summary of the main categories of market scrap and their typical contents of residuals. Car shredded and heavy scrap contains an average of 0.25% of copper.

Table 5 Main categories of market scrap with typical content of residual elements [8]



Category of market scrap			Chemical compositions after melting (%)				
			Cu	Sn	Ni	Cr	Zn*
Market scrap	Obsolete	Car shredded scrap	0.23	0.052	0.069	0.123	(0.050)
		Heavy scrap	0.234	0.017	0.070	0.130	(0.210)
		Can scrap	0.050	0.128	0.032	0.061	(0.00)
	Factory bundle		0.027	0.002	0.020	0.031	(0.70)
	Home scrap		0.021	0.01	0.050	0.030	(0.01)
Pig iron scrap			0.01	0.002	0.02	0.02	(0.002)

* Before melting

4.2 Residual elements in steel making

Figure 1 shows the different possible ways of production of steel from ore or scrap. The most usual way to process scrap is by melting in electric arc furnace (EAF). Scrap is also added into steel produced from ore in the oxygen furnace.

Long products are manufactures usually with EAF route, while BOF (basic oxygen furnace) plants mainly produce flat products.

Steel scrap makes for almost 100% of the iron-bearing charge in EAF steelmaking, while basic oxygen furnaces can process only up to 20% scrap.

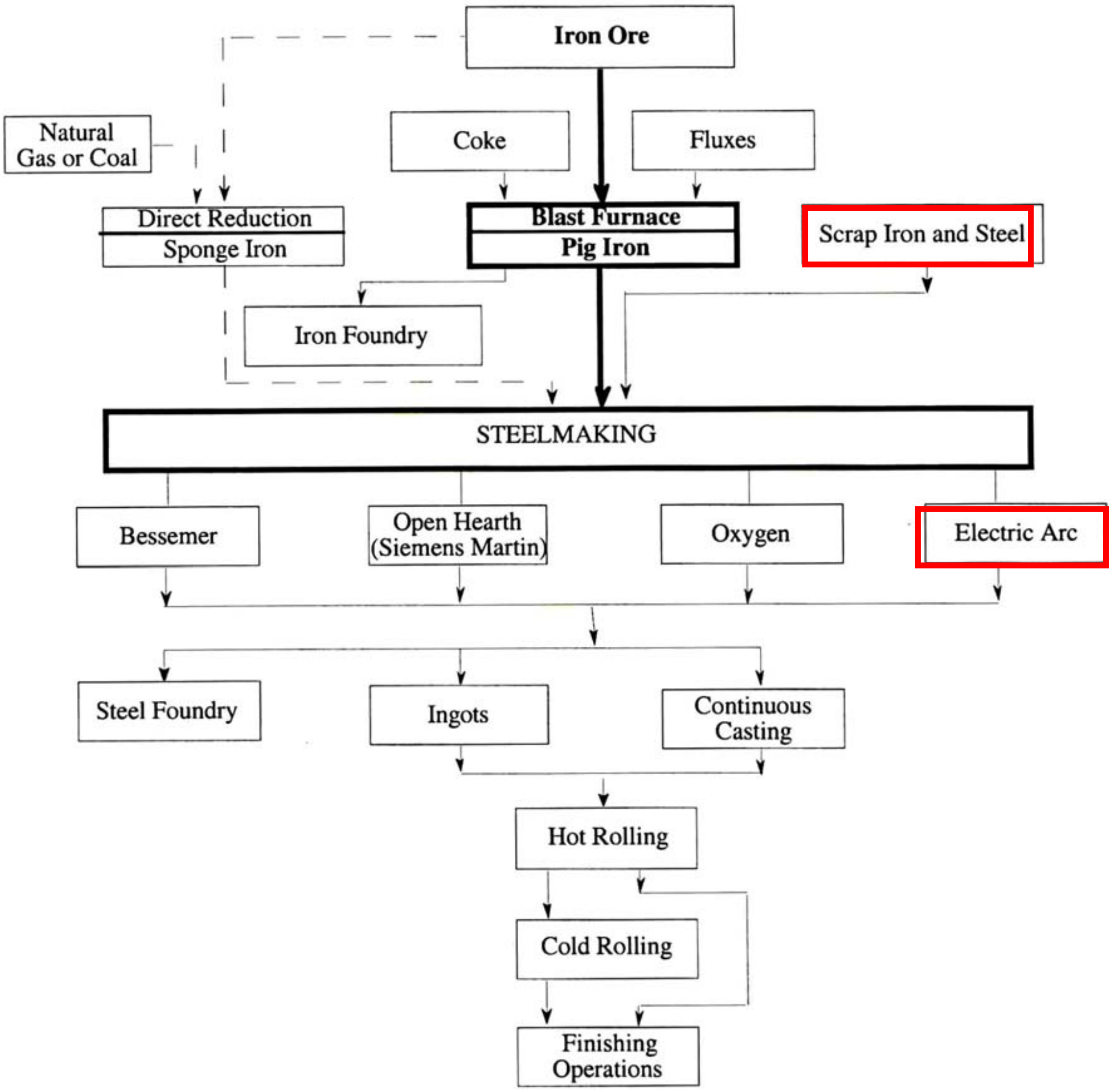
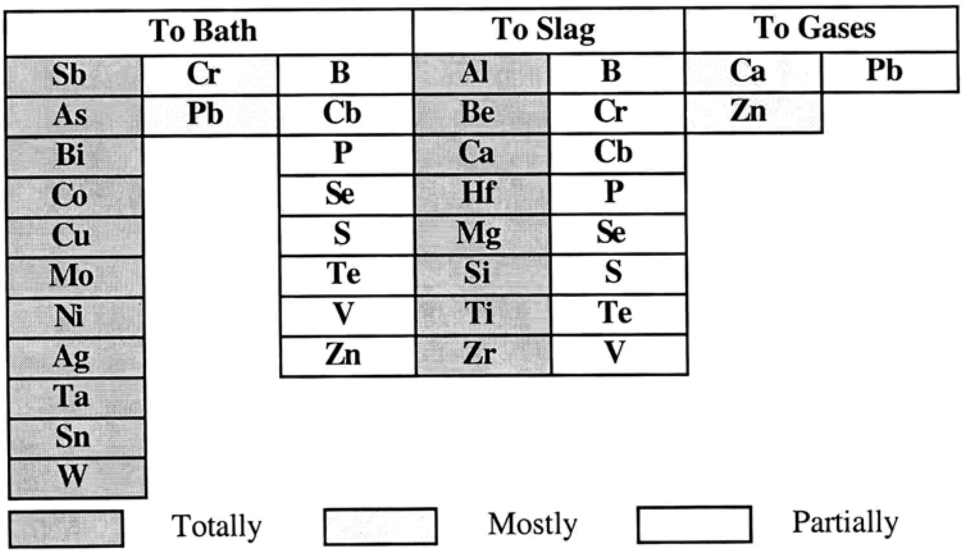


Figure 1 Iron and steel making processes [11]. The red marks show the most common way of processing scrap. It should be noted that recycled material containing large amounts of residuals are even often used in foundry to produce low-value cast iron products.

During melting operation, the different residual elements show different behaviours. Some mostly remain in molten steel while others mostly go to the slag or to gases. Figure 2 shows for the main residual elements a summary of these behaviours, which are related to the oxidation and reduction reactions of each element and to their physical state, see Figure 3. Note that **Figure 2** could be completed by adding Hg to the elements moving to gases.

Elements remaining in the molten steel bath are the one, which are most relevant to study when considering effects of residuals on steels products and down stream process.



To Bath			To Slag		To Gases	
Sb	Cr	B	Al	B	Ca	Pb
As	Pb	Cb	Be	Cr	Zn	
Bi		P	Ca	Cb		
Co		Se	Hf	P		
Cu		S	Mg	Se		
Mo		Te	Si	S		
Ni		V	Ti	Te		
Ag		Zn	Zr	V		
Ta						
Sn						
W						

Totally Mostly Partially

Figure 2 Some residual elements present in commercial grades and general behaviour under meltdown conditions in EAF operation [11].

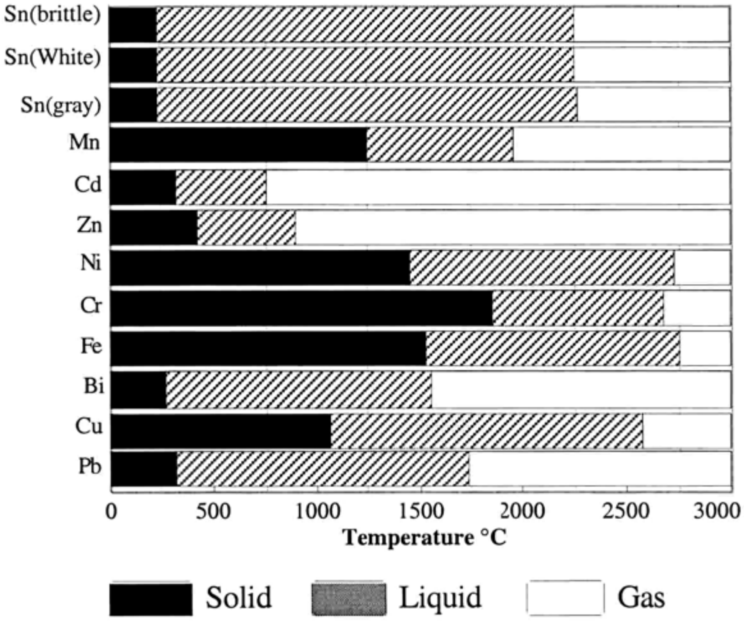


Figure 3 Physical states of some residual elements [11].

4.3 Removing of residual elements

Removing of residual elements is a broadly studied field, which is treated in many articles. As it is not the topic of this review, only some references are named here.

All of the various methods for the removal of residual elements from liquid steel or solid scrap are more or less costly and time-consuming steps in the production chain from scrap to steel. Different techniques of removal of residual elements are reviewed in reference [10]

Article [4] deals about how to remove the residuals elements copper and tin from steel scrap and change them into such form that they are stable and exert no adverse effect on the environment and presents the results of common work of two research groups in Japan.

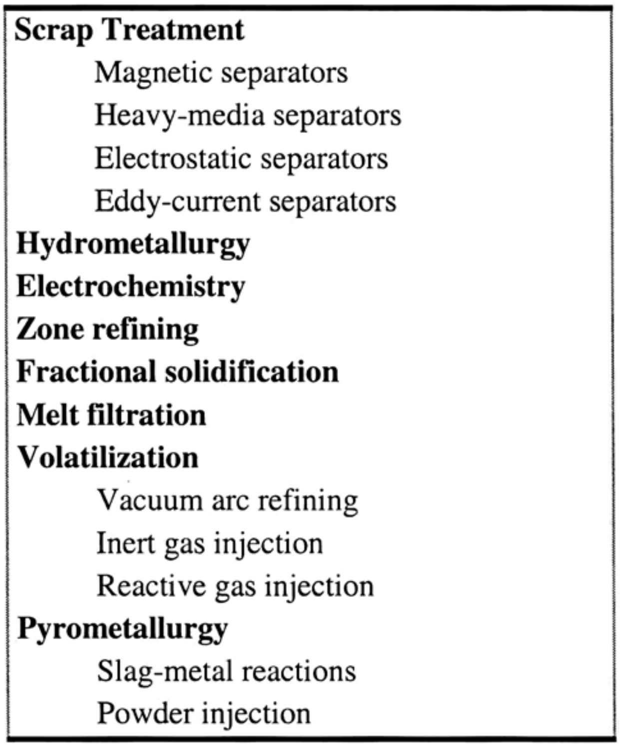
A number of technologies for removal of Cu are named in article [12] and a new way is proposed based on:

- oxidation of solid ferrous scrap in air or other oxidizing environments
- followed by fluxing of the copper oxide in the oxidized solid scrap by using molten slag at temperatures below steel scrap melting point.

The available thermodynamic data of the tramp elements in molten steel are summarized in reference [5]. The possibility of the removal of tramp elements from molten steel by using calcium-metal halide fluxes is thermodynamically estimated. The calcium-metal halidefluxes have an excellent refining ability.

Finally, Table 6 lists possible methods used to sort steel scrap and eventually to remove residual elements.

Table 6 Possible removal methods of residual elements [11]



- **Scrap Treatment**
  - Magnetic separators
  - Heavy-media separators
  - Electrostatic separators
  - Eddy-current separators
- **Hydrometallurgy**
- **Electrochemistry**
- **Zone refining**
- **Fractional solidification**
- **Melt filtration**
- **Volatilization**
  - Vacuum arc refining
  - Inert gas injection
  - Reactive gas injection
- **Pyrometallurgy**
  - Slag-metal reactions
  - Powder injection

4.4 Different modes of existence of residual elements

Reference [6] makes a distinction between residual elements, having an influence on the processing conditions and on the final mechanical properties of steel products, because of their presence in solid solution (mainly Mo, Cr, Ni, Cu) and because of their segregation at interfaces (mainly Cu, Sn, As, Sb). This is reviewed in this chapter.

Residual elements in solid solution

All metallic residual elements increase the strength/hardness and the hardenability of carbon and low alloy steels to different degrees when present in solid solution. hardness is related to the increase of strength when residuals are present in solid solution in the ferrite matrix while hardenability is related to the ability of the material to get hardened structures (bainite, martensite) when temperature treated.

The increase of hardeness is coupled with a general decrease in ductility. Toughness is little affected by Cr, Mo, Ni and Cu in solid solution excepted Ni which have a beneficial effect on the transition temperature of low-carbon ferritic steels.

As named, all metallic residual elements increase the hardenability of carbon and low alloy steels to different degrees when present in solid solution. Cr and Mo are the most efficient in this respect, Ni and Cu less. The effect of Cr is ambivalent and depends on the C concentration and its partioning between ferrite and carbides.

Residuals can also modify the microstructure of different phases. For eutectoid steels, Cr and Mo reduce the lamellar spacing of perlite. Cu reduces the degree of regularity of perlite and Ni has the opposite effect.

Precipitation

Residual elements can also precipitate and form inclusions in the steel matrix, alone or in combination with carbon (carbides), sulfur (sulfides) or N (nitrides). V, Nb, Ti, Zr, W, Mo, Cr and Mn are typical carbides builders and Mn and Ti are typical sulfide builders. The amount, distribution and size of the inclusions depends on the composition of the steel and on the treatment during down-stream process. Inclusions, if fine, mostly increase the hardness and strength of low alloyed steels. However, large inclusions can results in a more brittle material, and cause problems during production and final use.

Ti for example is used both as a dispersion hardener through the forming of titanium carbide particles, and as a sulphur binder to form hard sulphides and thereby improving cold working abilities. Titanium can also form precipitates that can act as nucleation sites for grains, contributing to a finer grain size.

Cu may precipitate at relatively high concentrations (>0,5%) during ageing treatment in the form of ε-Cu and thus impart a large increase in hardness. This effect is used in several steel grades (low alloyed steels used in the offshore, high resistance martensitic stainless steels). Increase of hardness depends on the Cu concentration in the steel, its degree of supersaturation and the time and temperature of ageing and of the preliminary structure of the steel.

Intergranular segregation

Residual elements may segregate to the grain boundary during cooling and coiling in the strip mill, or during final annealing after cold rolling. An important related aspect is the ability of the elements to reduce grain boundary cohesion, which makes fracture more likely. Of particular interest for interface segregation are solid solutions atoms with an atom size larger than the iron atoms. residuals elements such as Sn, Sb and As, are of prime importance, see Figure 4. Tin is reported to segregate to grain boundaries of thin steel sheet and P, Sb and Sn are reported to segregate in high strength C-Mn steels and provoque temper embrittlement.

The lower the carbon content of the steel, the greater the segregation of residual elements on grain boundaries. Ni, Mn and Cr enhance the segregation of residuals while Mo, Ti and rare earth can combat it.

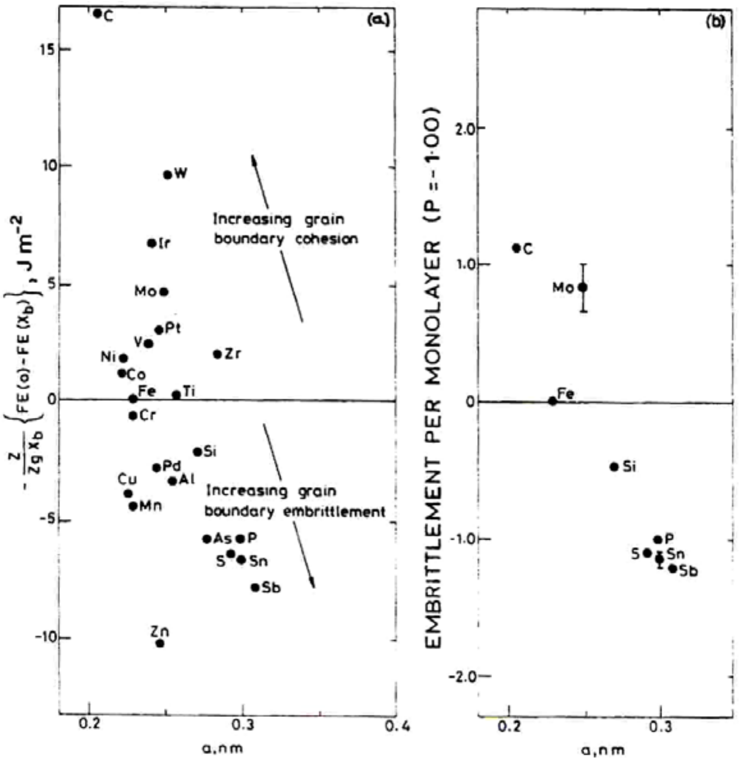


Figure 4 Relative grain boundary for different elements in iron at a given level of segregation. The more positive the ordinate value the more the element improves the grain-boundary cohesion and vice versa. (a) theoretical predictions. (b) experimental measurements.

Surface segregation

Surface hot-shortness is the result of the presence of liquid Cu at the scale-metal interface and the application of mechanical or thermo-mechanical stress. At high temperature the non-oxidized copper is progressively rejected at the scale-metal interface. Under oxidizing conditions and at concentrations of Cu no higher than 0,2%, the solubility limit of Cu in the austenite can be easily reached and Cu precipitates in liquid form, creating a liquid phase in the grain boundaries. The cracking severity is increased by the presence of other residuals elements such as Sn and Sb which lower the solubility of Cu as well as the melting temperature of the Cu-rich phase.

Nickel produces the reverse effect and is considered as the principal remedy against surface hot-shortness. Different studies present different values for the effect of Cu/Ni.

The addition of Si and Ni has some drawbacks, more adherent scale due to the presence of metallic Ni-rich phases which are mechanically anchored to the metal surface and create surface defects and increase wear of the process tools.

Segregation of Cu at the surface can however present certain advantage, which are useful in weathering steels [3]

The different nature of residual elements and their possible effects are summarised in Figure 5. This is developed in more details in following chapters.

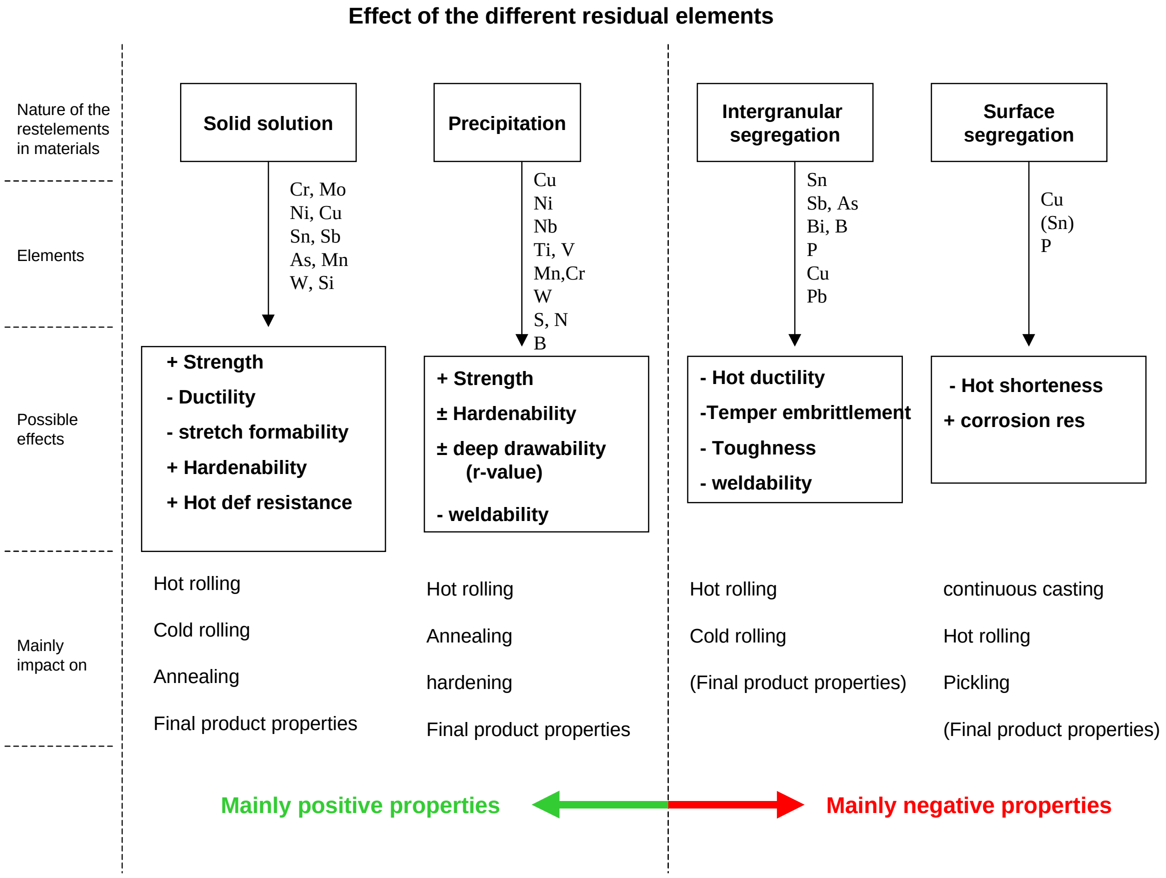


Figure 5 Overview of the nature of residual elements in steels and of their possible effects on down-stream process and end properties.

5. Influence of residual elements on down – stream process and end -properties

As a general statement, it is generally accepted that residual elements have a more pronounced effect on down-stream process and final properties for all applications that require low carbon clean steels than for the medium and high alloyed steels. (Extra low carbon ELC, low carbon LC and ultra low carbon ULC-IF).
The different steps of the down-stream processing, such as hot rolling, cold rolling, drawing, annealing, hardening, welding, and the final properties of the material are considered in this chapter. Tables summarizing the effects of residual elements given in literature are then presented in chapter 7.

5.1 Hot working

The general effect of residual elements in steel, in relation to the hot-working properties, has mostly been made in relation to copper. In reference [13] for example, it is stated that Cu is of main concern since, as a rule, if copper specifications are met the specifications for Sn, As and Sb are also met. This is because copper has been found to be the critical element in causing problems during hot-working (mainly hot-shortness) and has therefore been more extensively researched. In several cases however, it has been noted that copper have beneficial effects on the end products in regards to a finer grain structure and increased yield strengths. Consequently, this chapter is mostly discussing the influence of copper.

The influence of cooling rates and copper content on the microstructure of low carbon steel is shown in Figure **6**. The microstructure after hot-working has a direct effect on the mechanical properties of the steel and its behaviour during cold working.

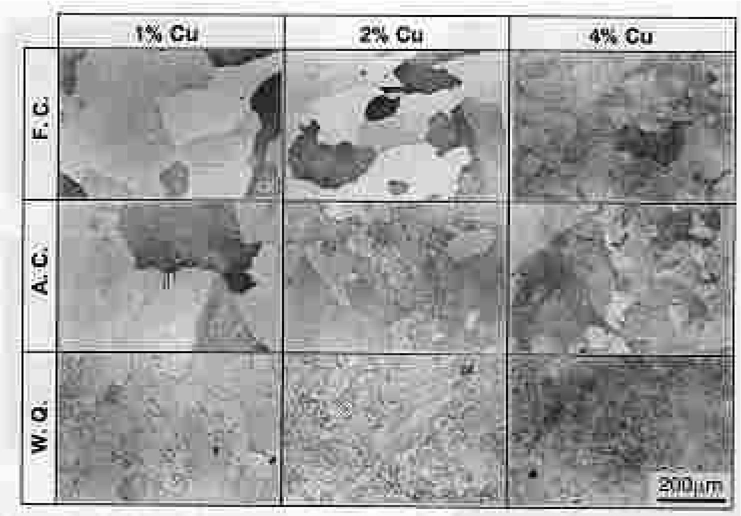


Figure 6 Differences in microstructure depending on cooling rate and copper content. The sample were solution treated at 1523 K for one hour and were either furnace cooled (F.C.), air cooled (A.C.) or water quenched (W.Q.) [14].

Only few studies show the effect of residual elements independently of copper. In reference [7], small additions of Sn, Mo, As and Cr were reported to modify the resistance to deformation during hot rolling of low carbon steels and ELC. Sn and Mo have the larger effect, while Cr and As show smaller effects (see Figure 7). The increase of the rolling force is to be related with a higher flow stress coupled with a retardation of the austenite recrystallisation. Therefore variations in residuals contents will do higher rolling loads and hence higher mill power consumption necessary, induce problems for the setup of the mills, and will contribute to a scatter of the steel properties

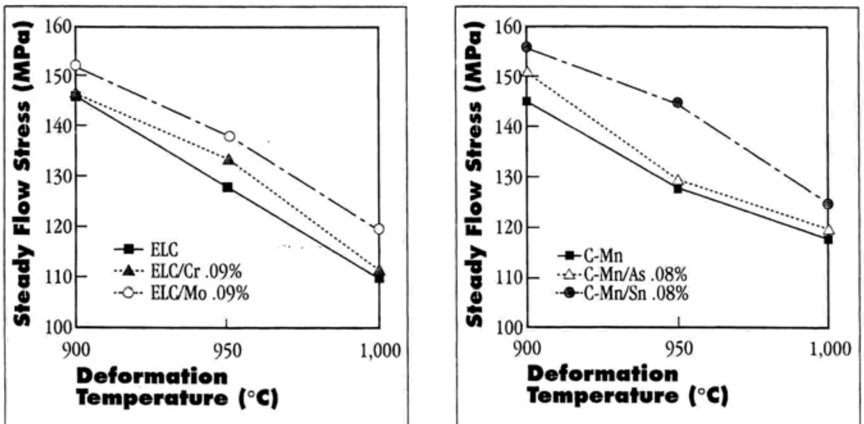


Figure 2 *Effects of Cr and Mo on the hot deformation resistance of ELC steel grades (0.02 percent C, 0.2 percent Mn and 0.05 percent Al).*

Figure 4 *Effects of Sn and As on the hot deformation resistance of ELC steel grades (0.02 percent C, 0.2 percent Mn and 0.05 percent Al).*

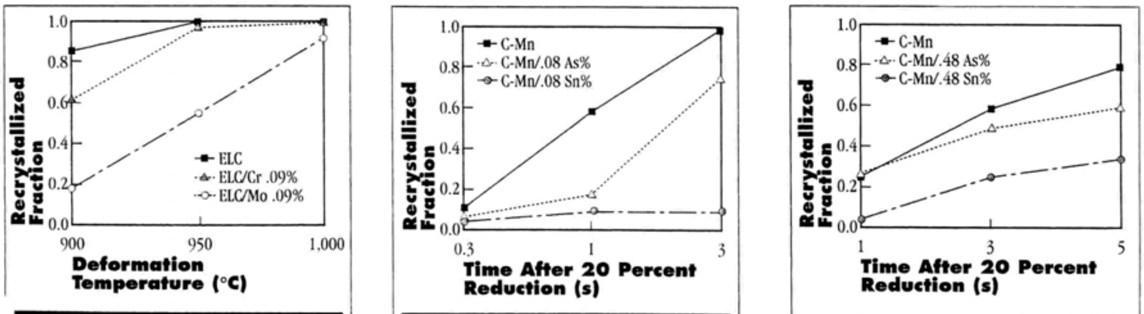


Figure 3 *Effects of Cr and Mo on the recrystallization delay in a hot deformation schedule on ELC steel grades (0.02 percent C, 0.2 percent Mn and 0.05 percent Al).*

Figure 5 *Effects of Sn and As on the recrystallization delay in a hot deformation schedule on ELC steel grades (0.02 percent C, 0.2 percent Mn and 0.05 percent Al).*

Figure 6 *Effects of Sn and As on the recrystallization delay in a hot deformation schedule of C-Mn steel grades (0.11 percent C, 0.9 percent Mn and 0.05 percent Al).*

Figure 7 Influence of residual elements on the resistance to deformation and recrystallisation during hot rolling.

5.1.1 Surface defects, hot-shortness

Effect of copper – hot-shortness

It is considered that copper is the key element related to surface defects of steel. The preferential oxidation of iron on the surface causes enrichment of Cu and then formed liquid Cu penetrates into the austenite grain boundaries to tear the grains, leading to a loss of ductility in the temperature range 1050-1200 [16]. This can occur for copper contents over 0.1 – 0.2 % and is called for hot-shortness. [17].

Due to preferential oxidation of Fe at the surface, Cu is enriched in the grain boundaries creating a liquid phase. The enriched phase becomes liquid over 1090 ^{o}C. The liquid can then infiltrate the austenite grain boundaries (Figure 8) causing severe cracking (Figure 9).

The solubility of copper in iron increases significantly with temperature increasing the dispersion of copper into the grains. At 1193^{o} C the solubility of copper in austenite is reported to be about 10 w% and about 0.1 w% at 521^{o} C [18]. Although increasing the temperature will also increase the rate of oxidation of the surface. The forming of the copper rich phase occurs mainly in the struggle of two competing forces: copper enrichment in the grain boundaries due to preferential oxidation of iron at the surface, and dispersion of copper in to the grains through diffusion [19]. As the temperature increases the dispersion of copper becomes dominant, at longer oxidation times a steady state is reached and the enrichment and dispersion rates of copper along the grain boundaries becomes constant. It has been found that there is a critical temperature where maximum cracking occurs that is dependent on copper content. However at temperatures above 1200^{o} C up to 1300^{o} C there was a marked reduction in surface cracking at Cu levels up to 0.39 w% [15] to the point where no cracking could be found. These results are consistent with observations of Cu-enrichment in metal/oxide interface of plain carbon steels.

It has also been found that there is a critical heating temperature where maximum cracking occurs that is directly related to copper content [15] (Figure 10).

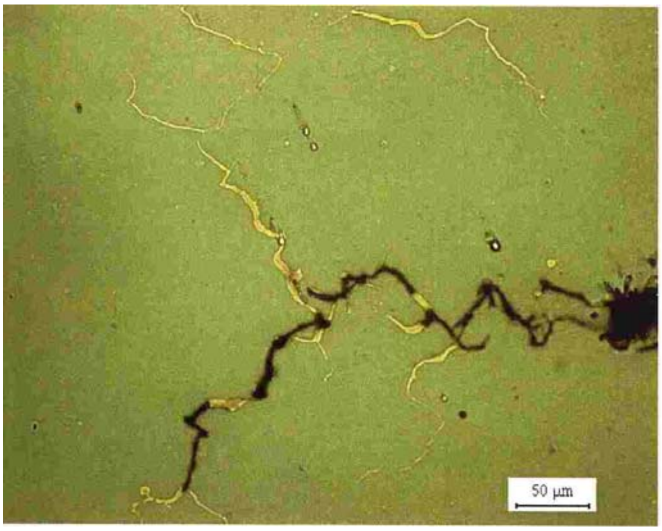


Figure 8 Cracks following austenite grain boundaries that has been infiltrated by liquid copper in a 2.5 w% Cu steel.

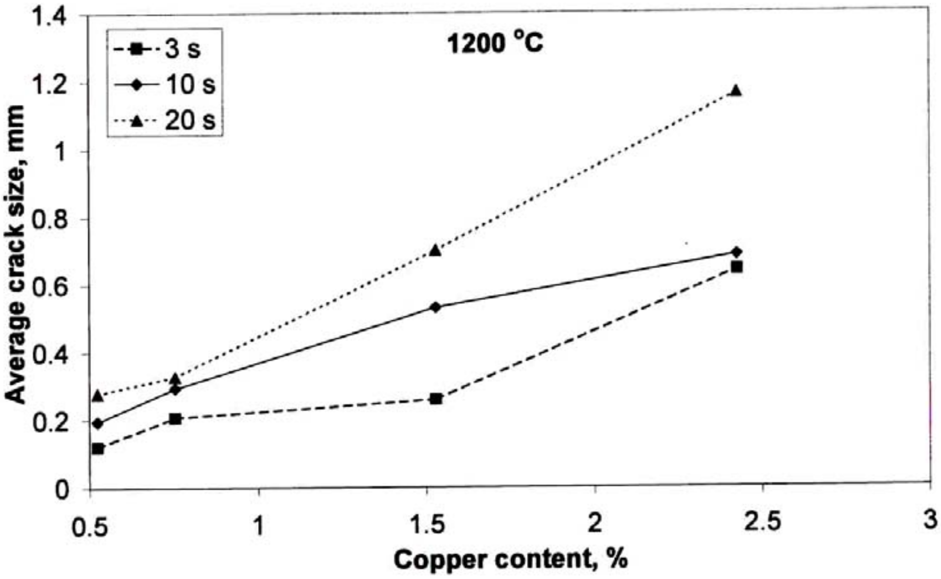


Figure 9 The effect of copper content on the average crack size in the hot ductility tests at varying oxidation times in air.

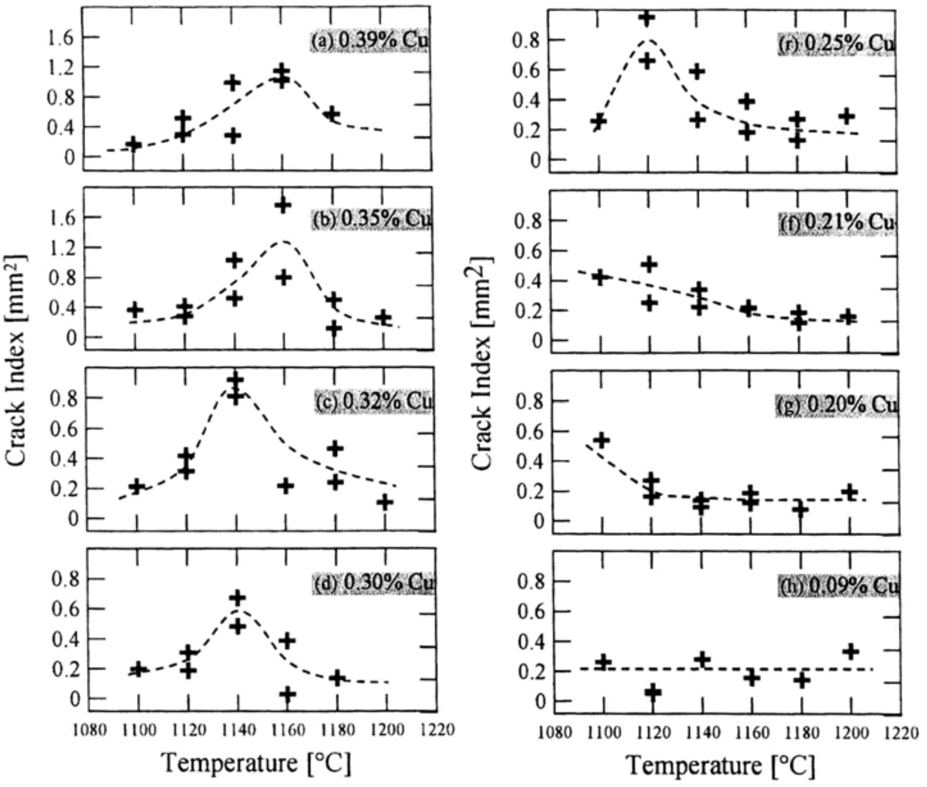


Figure 10 Crack index measurement for steels containing different levels of copper illustrating maximum cracking at a critical temperature. All samples were heated and oxidized for 10 min and deformed, cracking was then quantified by average crack surface area.

Different hot working steps – copper influence

A broad study of steel processing when Cu and Sn is added is presented in reference [3] This study is interesting to refer to more in details as it reviews in detail the different step of hot-working. It concludes that the complete production process from the steel shop to the wire drawing bench can accept levels as high as 0,8% Cu and 0.05% Sn. The different metallurgical phenomena related to residual elements seem to vary linearly with the increase in their contents. No discontinuity has been observed for copper levels between 0,15 and 0,8%. For low-carbon steels, the small effects for copper concentrations up to 0.35% can easily be compensated by minor process changes. Control of the re-heating process (atmosphere, T, t) offers way of reducing the intergranular brittleness induced by copper segregation.

The following observations were done for the different processing operations.

The cracks induced in engineering steels during **continuous casting** were intergranular in nature whose number increased with Cu content. The maximal crack depth was in the order of one γ grain. The cracks were preferentially located in the areas under mechanical stress, i.e. pinch roll or withdrawal roll. In the case where Ni was intentionally introduced, in the amount corresponding approximately to the Cu content, the billet had no cracks.

The most damaging conditions with respect to the surface product quality arise when secondary cooling induces a long hold time at 1100°C.

It is possible to suppress surface cracking by strong cooling after mould extraction. The process has two effects: avoids long holding time of the surface at 1100°C (ideal temperature for Cu segregation at scale-metal interface) and allows formation of a new finer and more equiaxed γ grain

The **reheating furnace** introduces two self-opposing characteristics where their relative importance depends on the mode of use. The furnace enables to some extent the rectification of pre-existing defects in the bloom, by consuming metal in primary oxidation. A long hold time is thus useful in reducing the number of cracks. Prolonged hold time can also give rise to a new array of low depth intergranular defects, which appears only in high Cu steels. This can be attributed to an enrichement in Cu of the scale-metal interface and possibly of the garin boundaries in the reheating furnace. The grain boundaries become sensitized and brittle and oxidize during the first passage through the rollers. This is function of the Cu content and process and can be adjusted so that it do not present an obstacle for processing.

The increase in oxidation rate with increasing tramp elements content has the advantageous effect of removing a thicker layer of the outer cracked metal. Higher heating temperatures, longer heating times or more oxidized furnace atmospheres also favour metal consumption. Removal of the cracks by this means however, induces new accumulation of Cu at the scale-metal interface.

Studies on wire rod in low carbon produced by **hot rolling**, consisting in mechanical studies, defect analysis and pickling resistance, were done.

Relative insensitiveness of the hot rolling process on the quality surface of billets was observed. New defects are created at the beginning of hot rolling, but their depth is limited to an acceptable range for copper contents up to 0,35%. Concerning the mechanical characteristics of wire rod, Cu affect tensile properties through solid solution strengthtening but the effect is small. 0.1wt% Cu increases the strength by some 8 Mpa. The increase in strength is accompanied by a small decrease in ductility: elongation is reduced by 0,3% with an addition of 0.1%wt Cu.

Chemical **pickling** and mechanical **descaling** was not affectde by the copper content of the wire rod.

Effect of the other residuals on copper hot-shortness

Other residual elements modify the effect of Cu on hot-shortness in a complex way. Several studies are defining a Cu equivalent that could have the form Cu + aSn + bSb – Ni, where a and b are constants ranking respectively from 5 to 10 and 8 to 10, according to different authors.

In reference [20], a similar equation was derived describing the hot shorteness tendency as a function of steel composition.

$$Cu_{equ} = \%Cu + 1/n\ [\ 0.4\ (5Mn+\%Cr) + 8\ (\%Sn+\%Sb) + 2\%As - \%Ni] \leq A$$

Where n is the number of elements in the equation and A is a value depending on experimental and production parameters and on the type of steel.

Reference [21] investigated the effect of alloying elements on the solubility of Cu in solid Fe. An addition of Co, Ni and Al results in an increase of the solubility of Cu, while that of V, Cr, Mn, Si and Sn decreases the solubility. Increasing the solubility of Cu may decrease hot-shortness as less copper should build a liquid film at the surface.

As seen in the equation above, the elements, which have stronger influence on Cu hot-shortness, and thus which are most extensively reviewed in literature, are Sn and Ni.

Tin in combination with Copper is highly detrimental for the susceptibility to hot-shortness in the steel. Tin lowers the melting point of the copper phase and decreases the solubility of copper in iron causing further enrichment [22]. However in low copper steels tin by itself does not seem to affect surface hot shortness and no significant enrichment seems to occur.

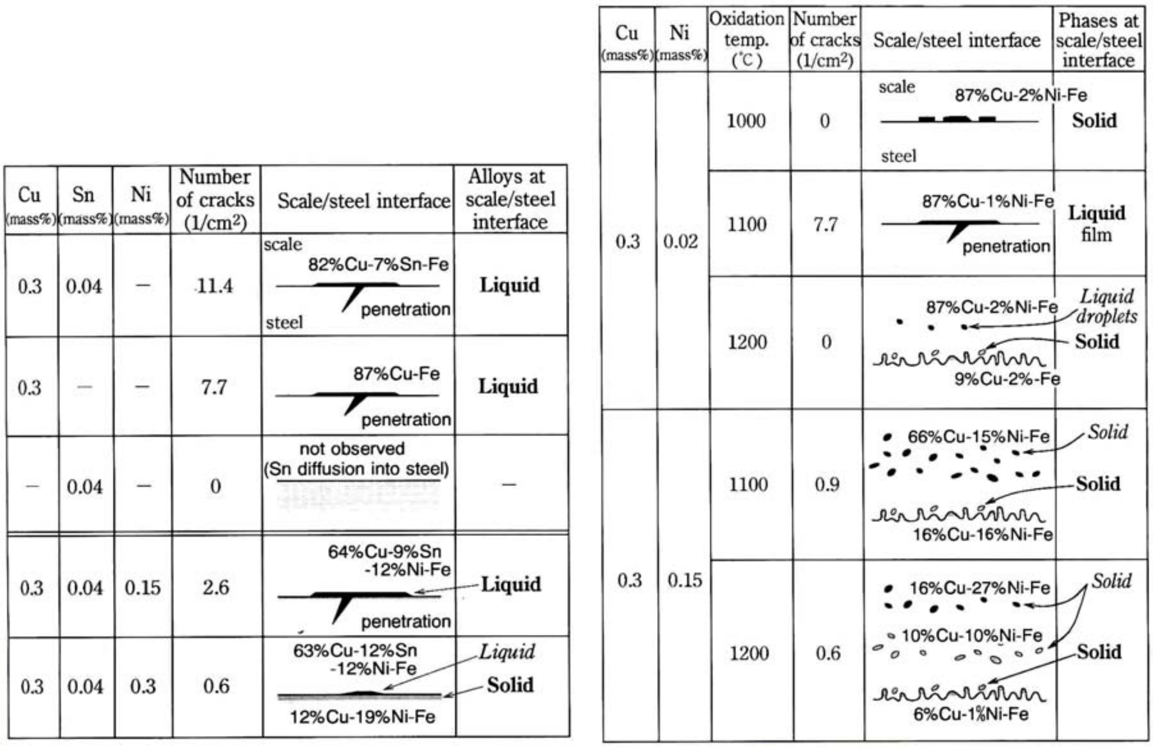
On the other side, Ni increases the solubility of Cu in iron lessening the susceptibility to hot-shortness. Ni affects the solubility of Cu in austenite and raises the melting point of the copper enriched phase. Adding 0.5 w% Ni to a low-carbon steel containing 0,5% Cu decreases the susceptibility to hot shortness. Moreover, in combination with an addition of 0.4 w% Si, only 0.26 w% Ni is needed to reach the same reduction of hot-shortness as if only 0.5 w% Ni is added. [22]

The effect of these three key-elements, Cu, Ni and Sn, on the hot-workability of mild steels was investigated and illustrated in papers [23] and [24] A hot rolling condition was simulated by oxidizing followed by tensile-deforming and the hot workability was assessed by measuring the number of surface cracks. The phases formed at the steel/scale interface were analysed and modelled, which is presented in Figure 11.

Sn as low as 0.04%increased the number of cracks in an 0.3% Cu bearing steel. Sn decrease the solubility limit for Cu in Fe, thus increasing the amount of liquid Cu enriched alloy and enhancing the surface cracking by Cu liquid embrittlement.

0.3% Ni supressed the cracking in an 0.3%Cu-0.04%Sn bearing steel. The phase calculation at an oxidation temperature 1100°C showed that the Cu and Ni enriched layer was solid. Therefore, the addition of 0.3%Ni suppressed the surface cracking in the Cu-Sn bearing steel.

For a 0.3%Cu bearing steel, the surface hot cracking occured only at 1100°C oxidation due to a liquid Cu enriched phase formed at the scale/steel interface. An addition of 0.15%Ni suppressed the surface cracking of 0.3%Cu bearing steel by eliminating all the Cu enriched liquid phases.



Cu (mass%)	Sn (mass%)	Ni (mass%)	Number of cracks (1/cm^2)	Scale/steel interface	Alloys at scale/steel interface
0.3	0.04	–	11.4	scale 82%Cu-7%Sn-Fe steel penetration	**Liquid**
0.3	–	–	7.7	87%Cu-Fe penetration	**Liquid**
–	0.04	–	0	not observed (Sn diffusion into steel)	–
0.3	0.04	0.15	2.6	64%Cu-9%Sn -12%Ni-Fe penetration	**Liquid**
0.3	0.04	0.3	0.6	63%Cu-12%Sn -12%Ni-Fe 12%Cu-19%Ni-Fe	*Liquid* **Solid**

Cu (mass%)	Ni (mass%)	Oxidation temp. (°C)	Number of cracks (1/cm^2)	Scale/steel interface	Phases at scale/steel interface
0.3	0.02	1000	0	scale 87%Cu-2%Ni-Fe steel	**Solid**
		1100	7.7	87%Cu-1%Ni-Fe penetration	**Liquid film**
		1200	0	87%Cu-2%Ni-Fe 9%Cu-2%-Fe	*Liquid droplets* **Solid**
0.3	0.15	1100	0.9	66%Cu-15%Ni-Fe 16%Cu-16%Ni-Fe	*Solid* **Solid**
		1200	0.6	16%Cu-27%Ni-Fe 10%Cu-10%Ni-Fe 6%Cu-1%Ni-Fe	*Solid* **Solid**

Figure 11 Relationship between Cu, Ni and Sn enriched phases and surface cracking

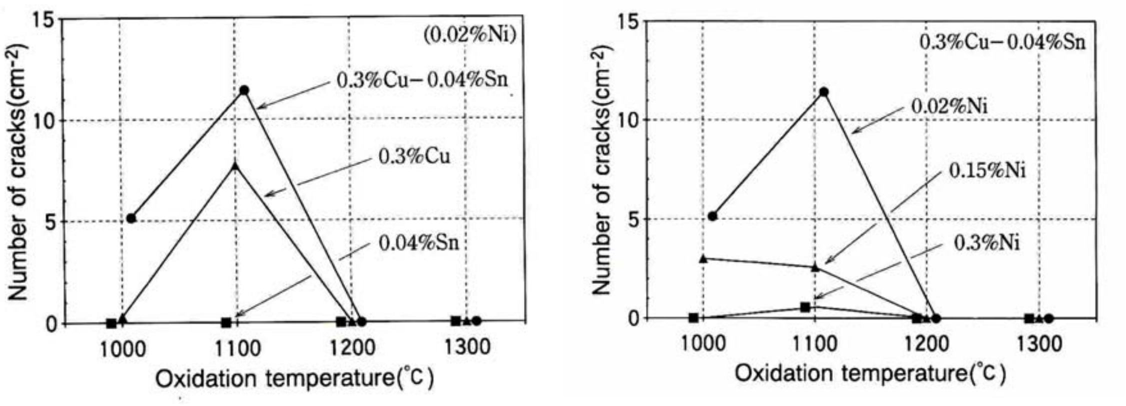


Figure 12 Influence of Cu, Ni and Sn on the surface cracking.

In reference [25] it was found that in 0.1 w% C steels, boron in amounts about 7 ppm seems to reduce the susceptibility to hot-shortness by altering the ability of the Cu phase to wet the surface of the austenite grain boundaries. One theory is that boron segregates to the grain boundaries and influences the surface boundary energy in the steel. However, to control the alloying to such an exact degree may be difficult.

The effects of Si and P on surface hot shortness due to Cu in low carbon steels are examined in reference [26] using a method based on tensile tests.

At 1100°C, single additions of 0.4%Si and 0.02%P were effective to decrease susceptibility to surface hot shortness, although these increased the oxidation rate. Duplex addition of 0.4%Si and 0.02%P decreased the oxidation rate and exhibited substantial effect on a decrease in the susceptibility. Addition of Si decreased the amount of Cu-enriched phase at steel/scale interface, which may be due to internal oxidation of Si. The forming of a molten phase of iron and silicon oxide in the scale can work favourably to occlude any liquid copper into the scale, not allowing it to penetrate the steel is also suggested. Si also contributes to a decrease in the growth rate of the crack created by the penetration.

Addition of P seems to increase slightly the amount of Cu-enriched phase.

A critical stress exists to fracture the specimens by Cu-enriched liquid phase. The additions of Si and P increase this critical stress.

The influence of silicon on the evaporation rate of copper has also been studied 27. The affinity of silicon to iron in the melt affects the activity of copper in the bath. The evaporation of copper from the bath was found to be promoted by the decarbonization of the melt that caused turbulence in the gas/metal interface.

Avoiding hot-shortness

In order to avoid surface hot shorteness, the experimental critical levels tolerated in steels have to be adapted according to the process conditions. Thus, the most common way to avoid the problem is to dilute the contaminated steels by virgin iron sources, but it is costly.

Reference [17] propose two solutions to avoid hot shortness, based on that it is due to the fact that the preferential oxidation of iron on the surface causes enrichment of Cu and then formed liquid Cu penetrates into the austenite grain boundaries to tear the grains.

The first solution is to avoid oxidation and mechanical stress at the temperature around 1150°C. The second is to enhance the heterogeneous nucleation of liquid Cu at MnS precipitates inside the austenite grains. The behaviour of the heterogeneous nucleation of ultra-fine Cu precipitates using Fe-10mass% Cu alloys with or without MnS are compared.

The Cu precipitates are classified into 3 types:

- Liquid Cu at the garin boundariesw
- Globular Cu particles nucleated at MnS or inclusions
- ε-Cu of the FCC structure in the size 20-200nm which may be effective for physical properties.

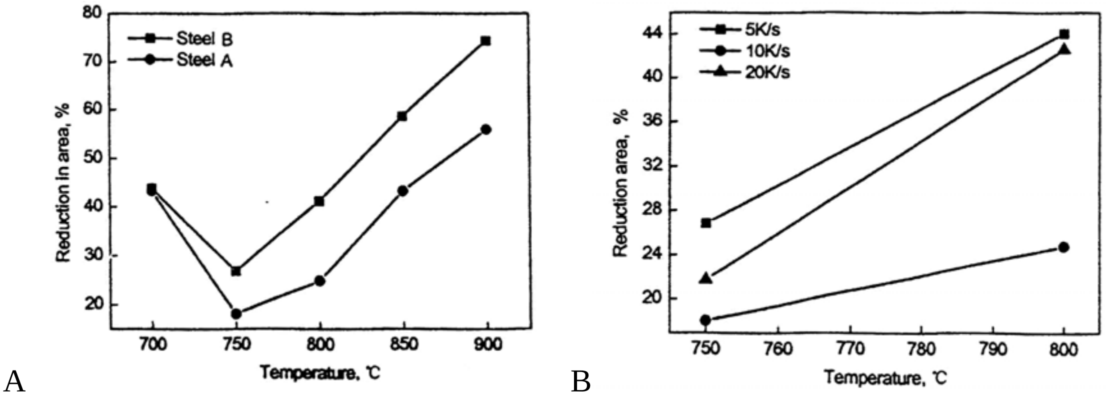
According to the authors, once the hot-shortness problem is solved, Cu or Sn may be utilized as effective micro-alloy elements.

Finally, reference [28] presents a review of russian studies on the effect of copper on structural steel and the problem of hot-shortness. Suppression of hot shorteness is achieved by introducing elements lessening the copper rich-phase and raising its melting point. Another direction is to change the heating and deformation temperature interval to decrease the oxidyzing power of the gas atmosphere and to shorten holding of the metal at high temperatures. Studies on different grades of structural steels showed that the allowable copper content in structural steels may be increased to 0,5%.

5.1.2 Grain boundary segregation

Low hot ductility in the temperature range 600-950°C met in some low carbon and low alloys steels is an industrial problem. Sn and also Cu are, even in that case, the critical elements.

The effect of Sn on the hot ductility of has been studied (continuous-casting thermal simulating tests). The hot ductility of a low carbon steel (0.15%) decreases with increasing Sn content and there is a trough in the RA-temperature curve, which is situated at 750°C (Figure 13 A). Non-equilibrium grain-boundary segregation of Sn produced during cooling is primarily responsible for the decrease in the hot ductility of the steel doped with Sn. There is a critical cooling rate for the tin segregation being between 5 and 20K/s at which the maximum segregation of Sn would be obtained (Figure 13 B).[30]



A B

Figure 13 A) Hot ductility curves for a cooling rate of 10K/s. B) Effect of the cooling rate on the hot ductility of steel B. Steel A and B are low-carbon steels, steel B contains 0.061% Sn whereas steel B contains less than 0,005% Sn.

In reference [31], the influence of Cu and Sn on the hot ductility at the strain rate of 10^{-3} for steels with C contents from 0.002 to 0.15%w was investigated. The hot ductility dropped at austenite + ferrite two phase region just below A_3, namely 800 to 900°C. The hot ductility deteriorated more at higher C content, and furthermore with the co-addition of Cu and/or Sn. It was considered that the deterioration at austenite + ferrite two phase region in the Cu, Sn bearing steel was caused by the combined effect of following factors:

- The formation of proeutectoid ferrite along the austenite grain boundaries.
- The segregation of Sn at the interface between proeutectoid ferrite and austenite or at the austenite grain boundaries.
- The increase in the difference of the deformation strength between austenite and proeutectoid ferrite.

5.1.3 Direct Strip Casting

Direct near-net shape casting is an attractive process for the production of sheet metal. Post-treatment (heating/rolling) is omitted and faster solidification rates may produce new microstructures. This process may have some advantages as one of the future approaches for the efficient utilisation of steel scraps because it considers the detrimental effect caused by the impurities in scraps, mostly hot-shortness caused by copper. Thus, a higher content of tramp elements (Cu, Sn) is tolerable without quality loss (surface cracking). Moreover, it has economical advantages.

A detailed description of the DSC (Direct Strip Casting) process, technical features, solutions, advantages and possibilities is given in reference [32], from which the schematical representations of a DSC pilot plant shown in Figure 14 are reproduced.

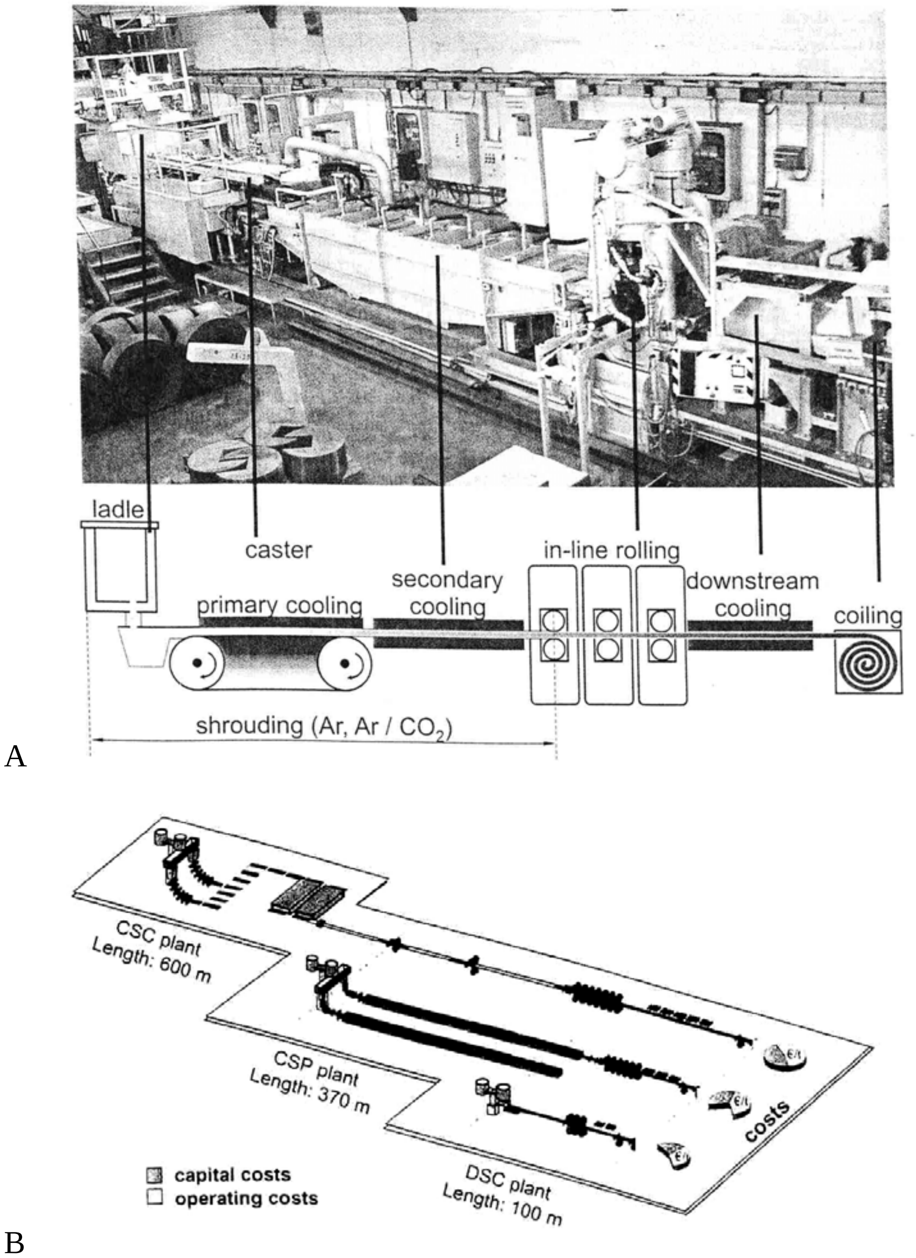


Figure 14 (A) DSC pilot plant. (B) Comparison of traditional and DSC casting plants.

Direct Strip Casting (DSC) is a method that combines short oxidation times with rapid cooling and direct rolling. This means that there is very little oxidation of the surface compared to conventional hot-rolling. Avoiding oxidation also means that there is less material loss and the enrichment of copper in the surface is avoided. From a ladle the melt is fed on to a water cooled conveyor belt. The sides are contained by water cooled copper blocks that move along with the melt in a block-chain [20]. The Ar/CO_2 protective gas is used as a rake to ensure a uniform distribution of the melt across the casting belt. The rapid cooling from the combination of the conveyor, acting as a continuous casting form, and the Ar/CO_2 gas rake makes it possible to produce steel grades previously considered to be infeasible. This method is currently only developed for flat products and has been tested for a width of 300 mm of the cast strip.

In order to investigate this method, difference in mechanical properties between direct cast and annealed strips of steel with high Cu, P and S contents were investigated in reference [33]. It was observed that the process produce fine microstructure and nano-scale copper sulfides. As cast and annealed have higher balance of strength and work hardening ability compared to strips without impurities.
As-cast strip has higher yield and tensile strength and maintains high work hardening ability at higher stress levels than that of the annealed strip. The nano-scale copper sulfide particles in the as-cast strip contributed most to the increase in yield strength.
It is finally believed that further improvements in strength and work hardening ability can be attained by controlling the particles size and the volume fraction in the strip.

A study was carried out at KIMAB and reported in reference [34] to ascertain how the situation could be improved when using strip casting in conjunction with direct hot rolling. This has included steels having copper contents up to 2.5% and in some cases also tin levels up to 0.1%. Laboratory simulations have been carried out to simulate the process conditions from the outlet of the strip caster through hot rolling, and the resulting materials have been examined with regard to their hot cracking behaviour and microstructural condition. Mechanical properties have also been measured on samples having different simulated coiling temperatures following hot deformation.
Susceptibility to hot cracking depends on the copper content of the steel and also on the process conditions of time, temperature and oxygen potential that apply after the strip exits the caster. Intermediate temperatures in the range 1100 - 1200°C are most dangerous and process windows for avoiding hot shortness can be defined on the basis of the present results, see Figure 15. In general, it should be possible to process steel containing much higher copper levels by strip casting than in current commercial production.
Copper-rich liquid films that penetrate the austenite grain boundaries are responsible for the loss of hot ductility in the steel surface. The presence of tin as an additional impurity to copper has not been found to be deleterious under the present conditions.
Conditions can be established to avoid hot shortness even in steel containing high copper contents, due to the short time that is available for oxidation
With sufficiently high contents of copper (above approximately 1%) precipitation occurs in ferrite leading to significant increase in strength in the final product and some reduction in total elongation. This strengthening, which is greatest when the steel is coiled at low temperatures in the vicinity of 450°C, could be well utilised in recycled steel manufactured from severely contaminated scrap. The refinement of the microstructure by precipitation of small copper particles (
Figure **17**) contributes to the hardening and strength by lowering the mean free path of dislocation travel.

Depending on the steel composition and coiling temperature it is possible to achieve very significant strengthening due to precipitation of copper-rich particles, see Figure 16.

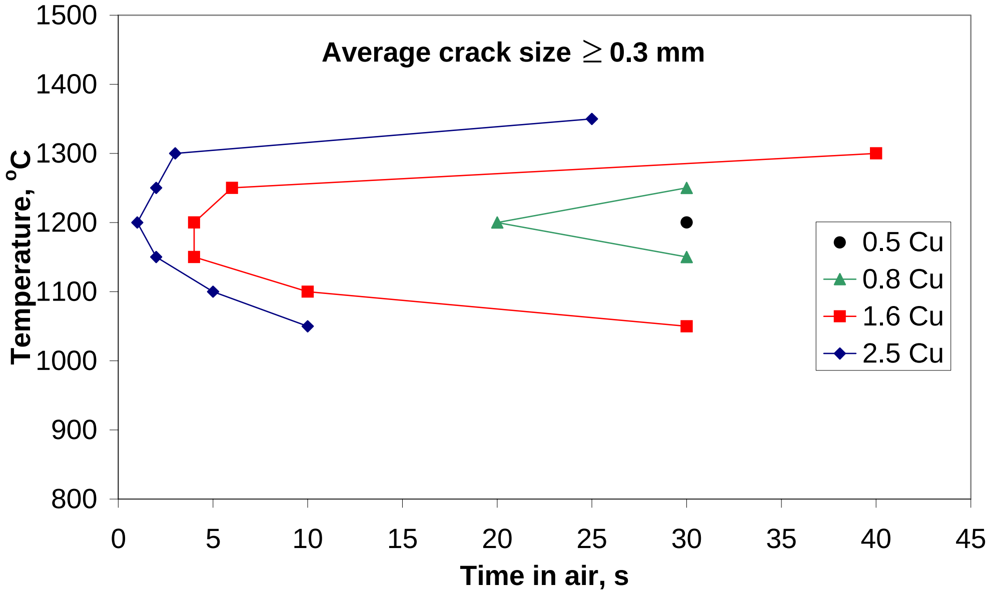


Figure 15 Compression temperature vs. time in air before hot deformation. The lines indicate when the cracks exceed 0.3 mm for the different steels

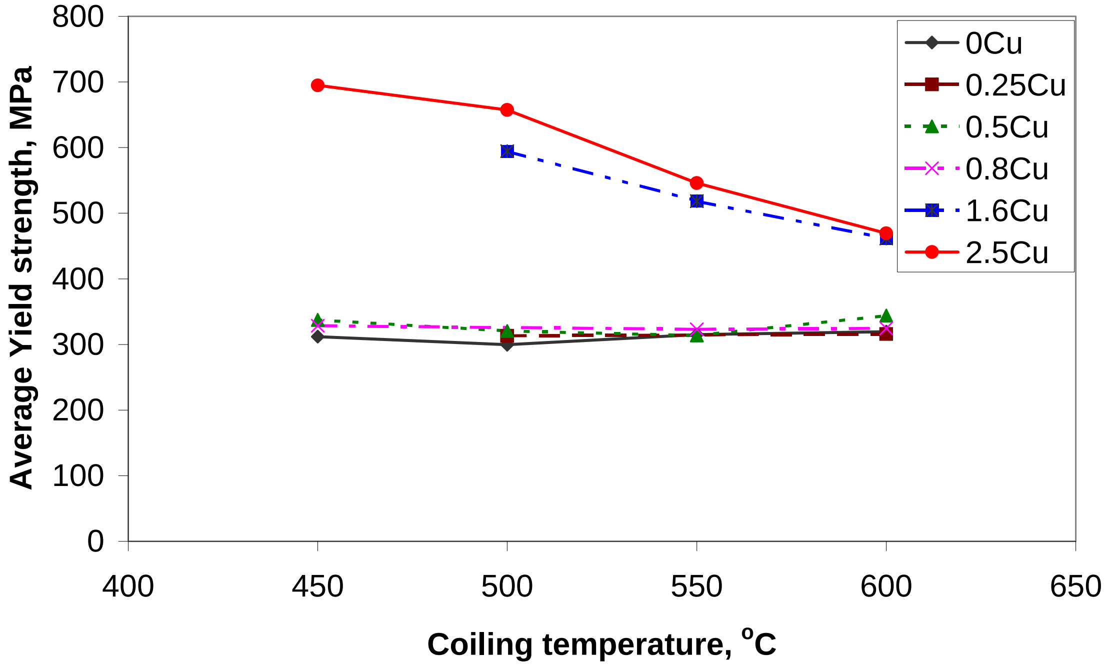


Figure 16 Yield strength vs. coiling temperature for steels with different copper contents

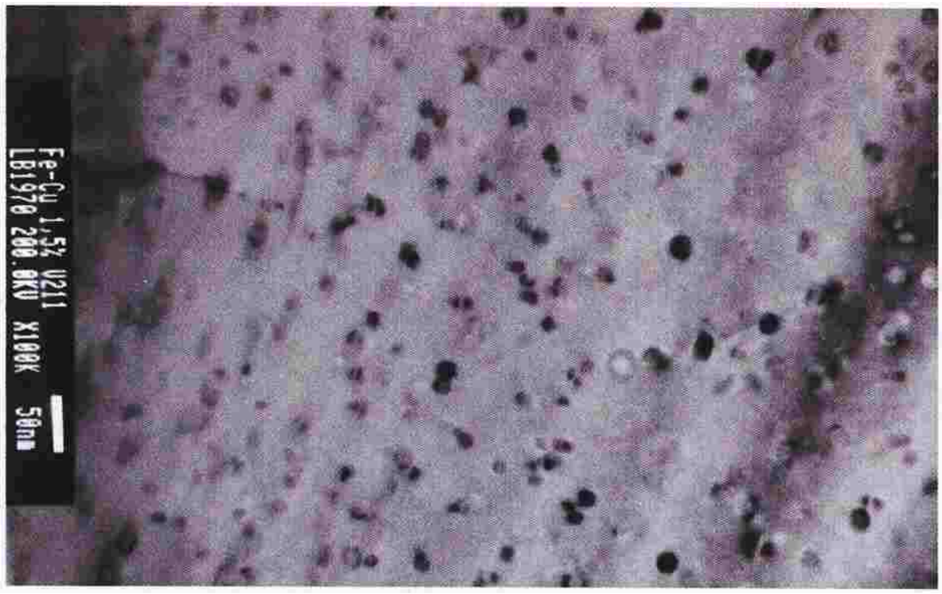


Figure 17 TEM picture of a 1.53 w% Cu alloyed steel after simulated hot rolling and coiling at 873 K . The dark spots are precipitates of ε-Cu 8-16 nm in size.

5.2 Cold working, Hardenability and end properties

Strength and final mechanical properties are often in close relation and inversely proportional with elongation and forming properties. Annealing and hardening is usually performed after cold-rolling. Residual elements affect in a complex way these different operations and parameters.
Which properties are desired and which amount of residual elements may be allowed depends on the type of steel, the production way and the aimed final use. A number of reported effects and limitations for residual elements with respect to cold working and hardenability, and effect on final strength, are given here.

5.2.1 Cold working

The material properties desired to favour cold working operations are often good elongation and drawability. The drawability of the material is quantified by the so-called r-value. The r-value is the quota between the contraction of the material in the width direction and the contraction of the material in the thickness direction.
In general, the harder the material the more likely it is to exhibit brittle behaviour while deformed, which is negative for cold working. Residual elements are mainly reported to contribute to hardening in some degree.

For materials intended for deep drawing or good formability, such as press sheets for car bodies etc, a low yield strength and long elongation are desirable. Thus, as reported in [16], Ni, Cr, Cu and Mo, which increase the resistance of cold rolled and annealed sheets, could become a problem for the production of soft drawable steel grades
Even reference [2] note that, for cold-rolled and annealed sheets, all residual elements, at the exception of Nb and Ti, adversely affect the crystallografic textures and partially the r-value (Lankford coefficient). Sn and As are the more detrimental in this respect (a significant effect is observed for a Sn content of 0.3%, see
Figure **19** A).

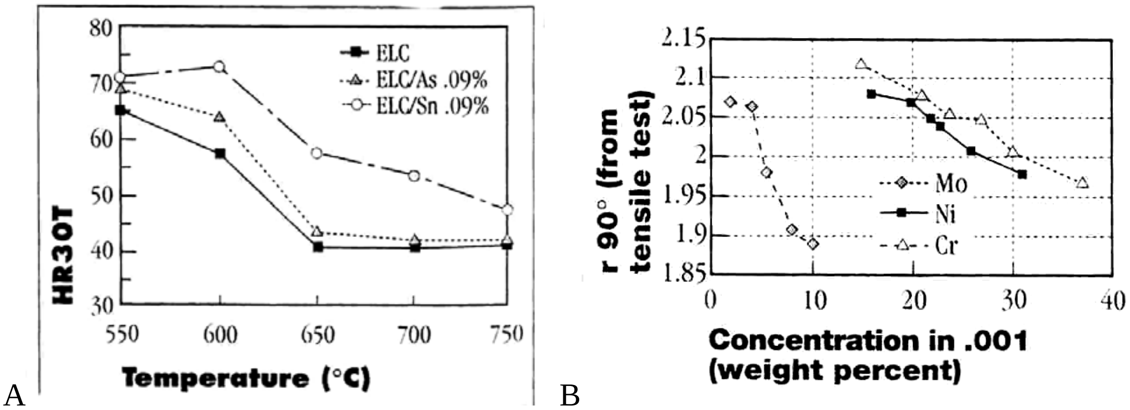


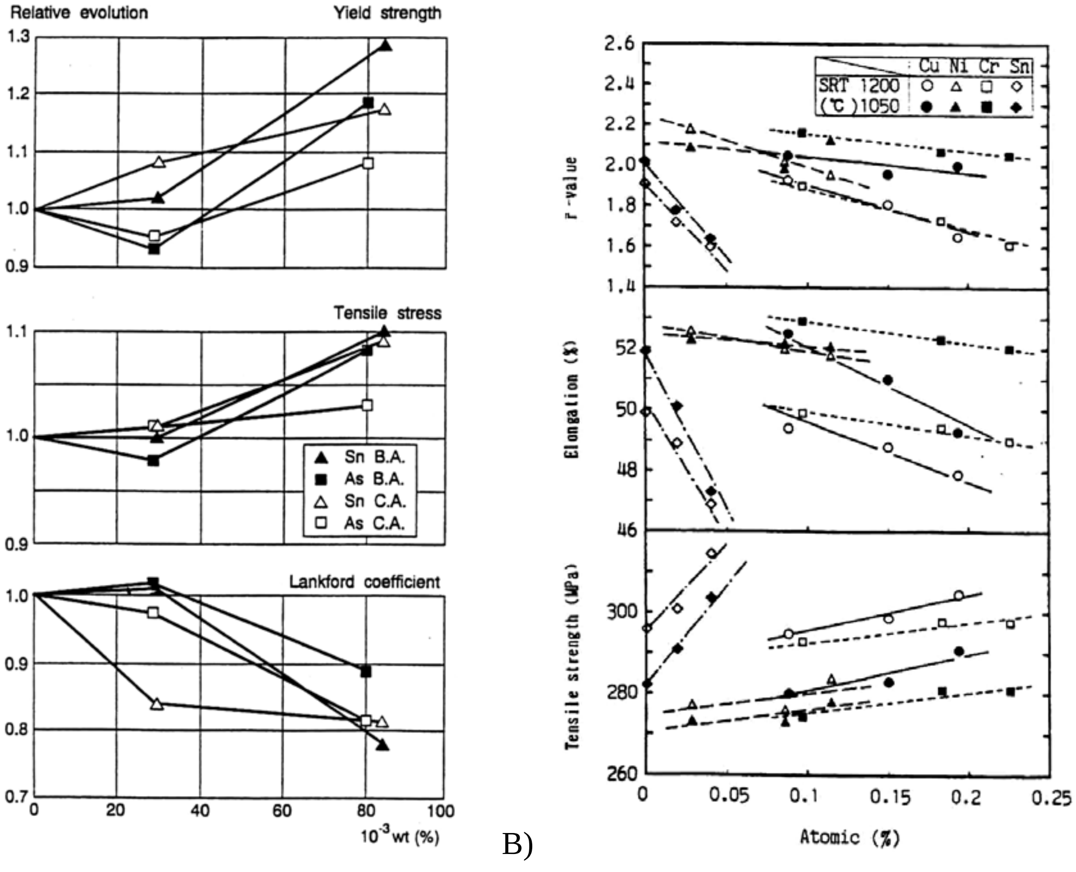
Figure 18 A)Effects of Sn and As on the recrystallization delay in a continuous annealing process on cold rolled ELC steel grades (0.02% C, 0.2% Mn, 0.05% Al, cold rolling 75%, continuous annealing, soaking for 1 minute). B) Effect of Cr, Ni and Mo on the drawability properties of 0.03% C steels (annealing temperature 680°C)

Sn, As, Cu, Ni, Cr and Mo have adverse effets on drawability, decreasing the r value and, to some extent, the ductility of ULC-IF and ELC grades (see Figure **18** B). [2].

Sn and As also have adverse effects on recristallization kinetics during the continuous annealing of cold rolled ELC steel grades (see Figure **18** A). The temperature for full recrystallisation increases, which implies that process conditions have to adapted to raise the annealing temperature. [16]

The tensile properties however were only little affected for residual elements up to 0.03%. However, a marked increase in tensile and yield stress was observed for concentrations of 0.08%. See Figure **19** for the effect of Sn and As.[2].

According to reference [3], Cu, Ni, Cr and Sn decrease grain size and increase solid solution hardening of thin steel sheet (IF Ti), thus decreasing anisotropy factor r and elongation (see Figure **19** B).



A) B)

Figure 19 A) Impact of residual elements on the mechanical properties of annealed cold-rolled sheets (BA = batch annealing, CA = continuous annealing).
B) relationship between atomic % and mechanical properties of Cu, Ni, Cr and Sn-containing titanium bearing extra low-carbon steel sheets.

In a study presented in reference [35], Cu and P bearing high strength cold rolled steel sheets with superior drawability have been developed. Cu and P contents are 0.6% and 0.08% respectively. The tensile strength of these steels are 500-550Mpa and the r-values are as high as 1.5-1.7. The excellent r-values are obtained by precipitation treatment of

650°C x 10h before cold rolling. Cu precipitates occured during heat treatment. Si and Mn strenghtened bearing steels are investigated. High Si steels have better elongation than high Mn steels. As to the r-value however, the latter are superior. In order to obtain excellent r-value, high reduction in cold rolling and slow heating in annealing are required in addition to the precipitation treatment before cold rolling (see Figure 20).

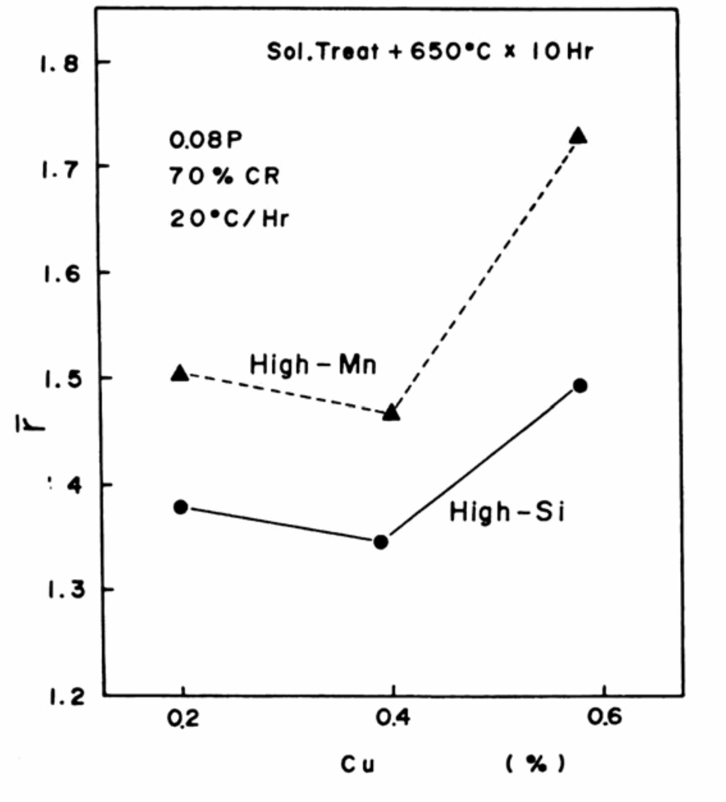


Figure 20 Effect of copper contents on r value

The cold-workability of low alloyed C-steels (XC10, XC42, 20M5) was studied in [39], and it was concluded that only Sn for concentrations higher than 0.04% and P for concentrations higher than 0.05% affect sensibly the ductility.

The effects of Cu (0.5%), Sn (0.12%) and Sb (0.11%) on tensile ductility and cold forgeability of a 0.5%C steel are investigated in [36]. The microstructures were not affected by the addition of Cu, Sn and Sb less than the contents given above. Similarly, these elements had no harmful effect on tensile properties and cold forgeability of the steels. The tempering at 500°C after quenching did not deteriorate cold forgeability of steels containing up to 0.1% Sb, and did not reveal an intergranular fracture on a cracked surface after upsetting test. Thus the authors state that cold forgeability of 0.5% C steel is mainly dominated by the existence of inclusions rather than by adding an impurity element of 0.5% Cu, 0.1% Sn or 0.1% Sb.

In a study made at KIMAB on the effects of copper on the properties of annealed thin sheet products, it was found that a moderate amount of copper in the material seemed to eliminate the Lüders elongation. This was only seen in material that had been batch annealed (

Figure **21** A). This effect was not seen in the continuously annealed specimen with the same copper content (
Figure **21** B). The elimination of the Lüders elongation is of interest for press sheets and steels that are intended for deep drawing and cold forming.

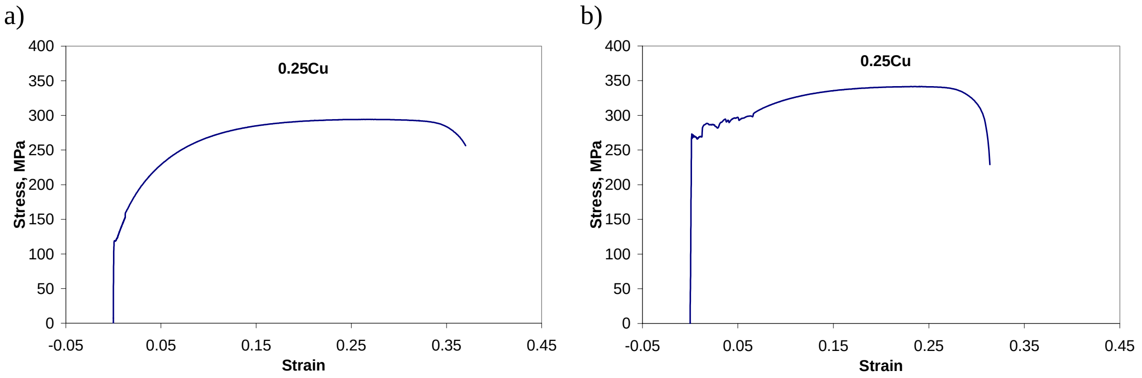


Figure 21 Stress-strain curve for a batch annealed steel, containing 0.25 w% Cu, showing no Lüders elongation. b) Stress-strain curve of same material as in a) but continuously annealed and showing a clear Lüders elongation.

Finally, almost no articles were found on the effect of residuals on machining of low alloyed steels. The effect of sulphur on machining, reported in [37], is mainly due to the formation of sulphides with other elements such as Mn. MnS can act as a nucleation site for microcracks, which raises stress in the material and further shear instability.

5.2.2 Hardenability

Reference [38] gives a summary of the most important variables, which influence hardenability, which are austenite grain size and composition, the second being discussed in this chapter.

Carbon has a marked influence on hardenability, but its use at higher levels is limited, because of the lack of toughness which results, the greater difficulties in fabrication and, most important, increased probability of distortion and cracking during heat treatment and welding.

Likewise, most metallic alloying elements slow down the ferrite and pearlite reactions, and so also increase hardenability. Exceptions are Co, because it increases the rate of nucleation and growth of pearlite, Ti because it reacts with C to form TiC and S because of MnS.

The most economical way of increasing the hardenability of plain carbon steel is to increase the manganese content, from 0.60 wt% to 1.40 wt%, giving a substantial improvement in hardenability. Chromium and molybdenum are also very effective, and amongst the cheaper alloying additions per unit of increased hardenabilily. Boron has a particularly large effect when it's added to fully deoxidized low carbon steel, even in concentrations of the order of 0.001%, and would be more widely used if its distribution in steel could be more easily controlled.

The effect of the main residual elements (Cu, Cr, Ni, Mo, P, Si, Sn) on the hardenability of low alloyed C-steels (XC10, XC42, 20M5) is also given in reference [39]. The effect on hardenability was ranked as follows: P>Mo>Cr>Si>Ni/Cu. The effect of Ni and Cu is neglectible under 0.3%. From that, it was assessed that elements coming from scrap (Cr, Si, Mo) allow enonomy of adding elements such as Cr, often necessary to increase hardenability of carbon steel produced from ore.

According to reference [28], copper somewhat increases the allotropic and martensite transformation temperatures, the increase of temperature being proportional to its content. As an element weakly stabilizing austenite, copper impedes the decomposition of austenite and thereby increases the hardenablility of steel.

In reference [40], the derivation of carbon equivalents to assess hardenability of steel has been examined. This equivalent was derived from the incubation time before the transformation to ferrite, pearlite or bainite, which is illustrated in **Figure 22** and is given in the equation below (note that the 1,8 is written 1·8 and so on):

$$\%C_{\mathrm{eq,cal}} = \%C + \frac{\%Si}{38} + \frac{\%Mn}{6{\cdot}0} + \frac{\%Cr}{1{\cdot}8} + \frac{\%Mo}{2{\cdot}3} + \frac{\%Ni}{12} + \frac{\%Cu}{9{\cdot}1} \quad . \; . \; . \; . \; . \; . \; . \; .$$

It was compared with experimental results from other studies, which is shown in **Table 7**:
The comparison reveals that the calculated coefficients for silicon, manganese, copper and nickel in the carbon equivalent equation are in good agreement with the experiments, whereas the agreement for the molybdenum and chromium coefficients is poor.

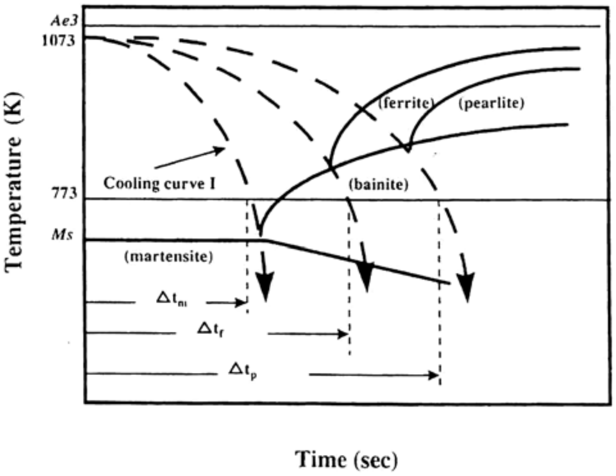


Figure 22 Critical cooling curves for ferrite, pearlite and bainite transformations on CCT diagram.

Table 7 Summary of coefficients for alloying elements in carbon equivalent equation.
(Note that the 1,8 is written 1·8 and so on).

Element	A_X	A_X/A_C in %$C_{eq,cal}$ (equation (12))	%C_{eq} (Bastien) (equation (15))	%C_{eq} (Yurioka) (equation (16))
C	−3·02	1	1	1
Si	−0·08	1/38	…	1/24
Mn	−0·50	1/6·0	1/4·1	1/6·0
Cr	−1·64	1/1·8	1/8·5	1/8·0
Mo	−1·30	1/2·3	1/6·5	1/4·0
Ni	−0·25	1/12	1/7·9	1/12
Cu	−0·33	1/9·1	…	1/15
N	0·087	−1/35	…	…

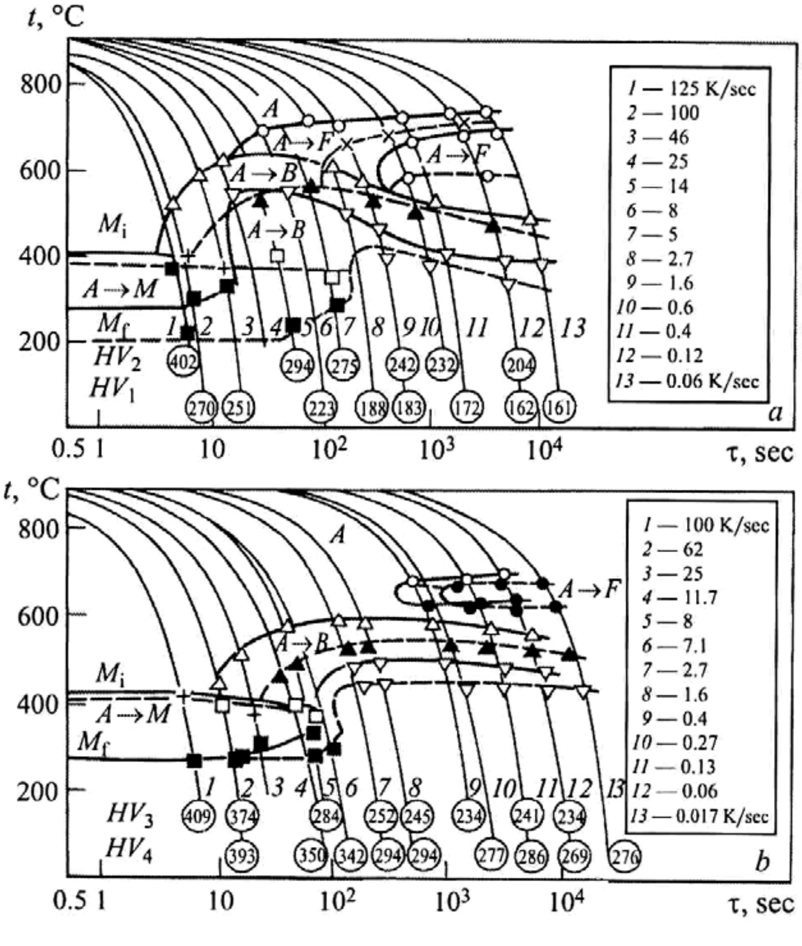
In reference [41], the influence of copper on quenching of high strength low alloy steels with 1.6% Cu, which composition is given in Table 8, is discussed.

Table 8 Composition of the steel studied in reference [41].

C	Mn	Ni	Cr	Cu	Mo	Nb	Si	Al	N	P	S
0.036	0.91	3.59	0.59	1.60	0.59	0.025	0.24	0.022	0.0097	0.008	0.005

An austenitizing temperature of 900°C was used, which allows to have all Cu in solution. On quenching from this temperature, a supersaturated solid solution was obtained with all of the Cu in solid solution in martensite. Cu slightly lowers the allotropic and Ms (martensitic start) temperatures, the extent being proportional to the Cu content. In addition, other solute elements present in the steel (especially Ni) are also considered to be austenite stabilizing elements. Therefore the decomposition of the austenite in such a steel is delayed. Because of the very low carbon content of this steel, only highly dislocated lath martensite structure was observed. Further discussion on the effect of Cu on properties from this reference is given in the next chapter.

Reference [42] is dealing with shipbuilding high-strength steels, which should provide high strength, ductility, and toughness in combination with a high resistance to brittle fracture and a good weldability. It is stated that when the carbon content is diminished in order to improve weldability, complex alloying becomes very important for the provision of hardenability, elimination of the formation of ferrite-pearlite structures, hardening and elevation of the resistance to brittle fracture. The complex effect of alloying elements in low-carbon heat-treatable Cr – Ni – Cu – Mo steel on the phase transformations that occur in quenching and tempering was studied. Results as well as the corresponding compositions are shown in Figure 23.



Heats	Content of elements, %*								M_i, °C	Ac_1, °C	Ac_3, °C	P_{cm}^{**}
	C	Si	Mn	Cr	Ni	Mo	Cu	V				
1	0.12	0.34	0.62	1.07	2.00	0.17	0.49	0.07	410	730	860	0.291
2	0.07	0.30	0.41	0.42	1.92	0.30	0.46	0.02	410	740	855	0.199
3	0.11	0.40	0.48	–	2.70	0.50	0.61	0.02	406	721	836	0.258
4	0.12	0.31	0.37	0.71	2.73	0.40	0.62	0.03	403	727	840	0.290

* The metal of the studied heats contained 0.008 – 0.01% sulfur, 0.005 – 0.013% phosphorus, 0.01 – 0.06% aluminum, and 0.03% calcium (as calculated).

** $P_{cm} = C + \frac{Mn + Cr + Cu}{20} + \frac{Mo}{15} + \frac{Ni}{60} + \frac{Si}{30} + \frac{V}{10}$.

Figure 23 Thermokinetic diagrams of low-carbon Cr-Ni-Cu-Mo steels with various contents of C and Cr. HV1-4 given in figures a and b correspond to the compositions of heat 1-4.

Quenching causes the formation of a composite martensitic - bainitic structure with predominant lath martensite, lower bainite, and bainite without visible carbide phase

segregations. 0.4% of Mo added suppresses the segregation of ferrite. Cr between 0.7-1.1% decreases the critical cooling rate in the intermediate range; in combination with 3% Ni and 0.3-0.5% Mo, it provides the formation of a martensitic – bainitic structure.
By reducing the concentration of C to 0.07%, Cr to 0.4% and Ni to 2%, baintic structures will be formed. These structures posses an elevated resistance to tempering as compared to steels quenched for martensite, are characterized by a high level of strength and posses a quite high resistance to brittle fracture. This makes it possible to have a high-strength Cr – Ni – Cu - Mo steel bearing 0.06-0.07%C with a bainitic structure that provides an excellent weldability without heating at a yield strength of up to 700 Mpa.

Finally, the 2 following studies present some more fundamental research on the effects of Cu addition on the structure and transformation of steel, for isothermal transformation and during cooling, which is even relevant considering hardenability.
In reference [43], the effects of Cu addition on the isothermal transformation behaviour and the transformed structure have been investigated in Fe-1.48Mn-0.48Si-0.15C-(0, 1.51)Cu % wt steels. The transformation behaviour, was shown to be retarded by the addition of Cu in the temperature range of 873 to 973K. The isothermally transformed structure at 903K is mainly acicular ferrite in 0 Cu steel, but is equiaxed ferrite with lots of subgrains in 1.5% Cu steel. Both the nucleation rate and growth rate of ferrite are decreased by the addition of Cu and this is considered to be caused by the reduction in austenite grain boundary energy due to segregation of Cu and the solute drag effect by Cu.

In article [44], Fe-(0.5-4)w %Cu alloys were cooled from γ field under various cooling conditions and phase transformation mechanisms were investigated.
In all of the cooling conditions, hardness of the alloys becomes higher with increasing Cu content. Effect of cooling conditions on hardness tends to be significant in alloys with Cu more than 1 wt %. Strength of alloys depends not only on a difference of matrix, martensite or ferrite, but also on dispersion of ε-Cu particles. In the case of air cooling for a Fe-4mass%Cu alloy, the alloy undergoes preferentially $\gamma \rightarrow \alpha$ massive transformation and then ε-Cu particles precipitates finely within the massive ferrite matrix. This leads to a large strengthening with a moderate ductility. Strength of Cu bearing steels can easily be controlled by varying cooling condition after a solution-treatment: steels are soft enough to be deformed and machined after furnace cooling, but strengthened after resolution-treatment followed by air-cooling.

5.2.3 End-properties

Tensile properties, strength

In reference [6], which reviews the influence of residual elements on mechanical properties of low-carbon steels, it is observed that all residual elements increase strength and decrease ductility and drawing properties. These effects are more pronounced for low carbon clean steels (low-carbon, extra low carbon and ULC-IF steel grades) than for medium and high carbon steel grades.
For cold rolled and annealed sheet, the major part of the product mix is low carbon or ULC steel. These steel grades are very sensitive to the content of residual elements. Sn, Cu, Ni and Cr increases the tensile strength of ULC-Ti steel grades and decrease their ductility (elongation). Sn, As, Cu, Ni and Mo decrease ductility of ULC-IF and ELC.

Thereafter are presented results of studies about mechanical properties on specific types of LC steels.

The effects of some residual elements on the properties of low carbon steel sheets containing titanium are reported in reference [45]. Copper specifically lowers the elongation of the material and increases the yield strength (Figure 24 A) while contributing to a refinement of the microstructure Tin increases the tensile strength of and lowers elongation and r-value (Figure 24 B). A refinement of the grain size was observed with increasing tin content. The change in tensile strength was reported to be approximately 45 MPa / 0.1 w% tin. Tin has a larger difference in atomic radius versus iron compared to copper, nickel and chromium. This causes tin to have a larger effect in both solid solution and as a precipitate.
The influence of nickel is at about the same magnitude as copper with respect to tensile strength increase. Only minor influences on elongation and r-value were observed at varying nickel content and at different heating temperatures, though the small changes is likely closer related to the low carbon content in combination with the presence of titanium. In total the influence of nickel contents up to 0.12 w% have little effects on the mechanical properties of low-carbon titanium containing steel sheet.

The effect of residuals on tensile properties and microstructure of low-carbon (0.04%) and medium carbon (0.2%) steel grades was studied in [46]. An increase in tensile strength and a slight decrease in ductility (combination of solid solution hardening and grain refinement) was observed for both types of steel The high tensile strength of steel containing more Mn and Si is thought to be mainly associated with increased pearlite content. For low carbon steels, the ferrite grain-size decreases from 24 to 18,5 µm for 0.04%Sn. But further addition (0.08%Sn and 0.05%P) and addition of 1.2%Mn and 0.3% Si only slightly decrease ferrite grain-size. For medium C steels (with 1.2%Mn and 0.3% Si), the ferrite grain-size decreases from 14 to 10µm for residuals increasing (0.08%Sn, 0.4%Cu, 0.4%Ni).

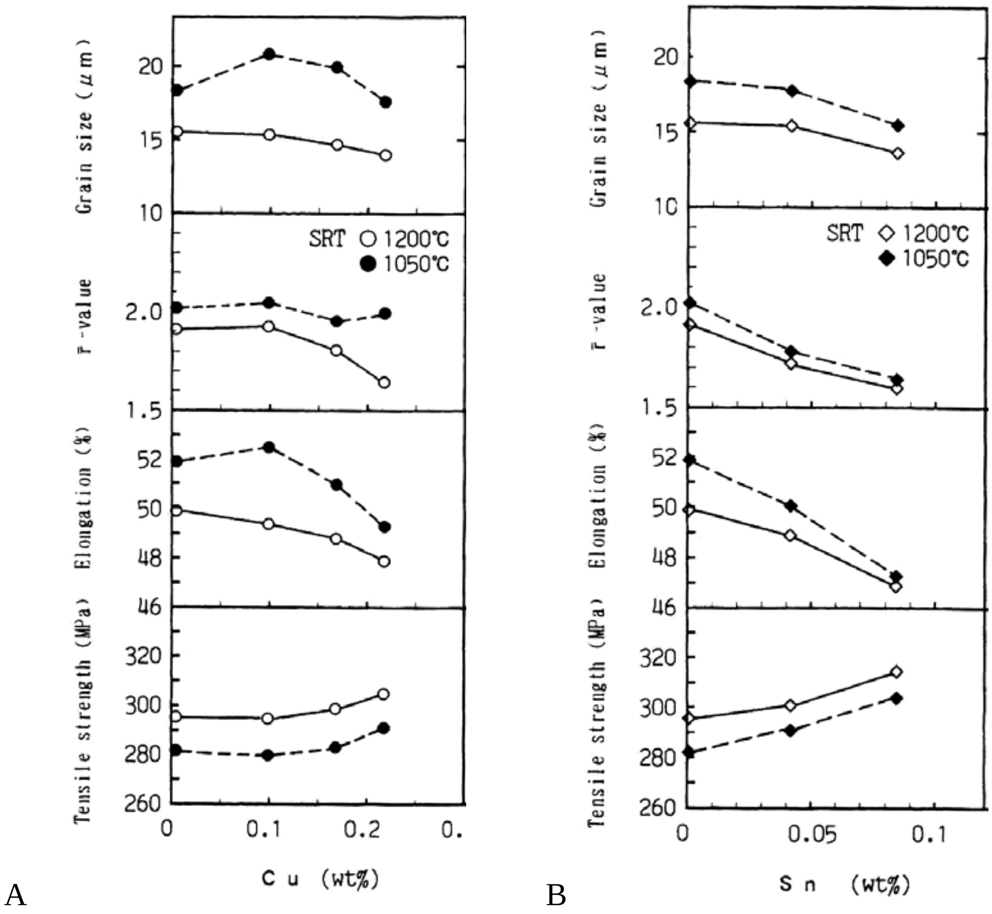


Figure 24 A) Mechanical properties as a function of copper content in titanium-bearing extralow-carbon steel sheets. B) Influence of tin on mechanical properties in titanium-bearing extralow-carbon steel sheets.

The properties of steels with additions of Cu (0.5%), Cr (0.4%) and Ni (0.4%) to the basic composition of 0.2C-1.5Mn-1.5Si were investigated in reference. [47] for high strength hot-rolled plates and [48] for TRIP-aided cold-rolled sheets.
The microstructures and mechanical properties of high strength hot-rolled steel plates were investigated in reference [47] for different coiling temperatures.

- When coiling temperature (CT) is low (around MS point), the fraction of retained austenite is low. Steel with additions of Cr (alone or with Ni) have % of retained austenite above 10%, but show the characteristics of dual phase steels, whereas when Cr is not added a discontinual yielded is observed.
- At CT = 450°C, retained austenite increase. Compared with CT400, tensile strength increase or maintains at the same level and elongation improves to greatly enhance the strength-elongation balance.
- When Cr is added as a tramp element, it works favorably for the formation of retained austenite at low CT. However, because of the increased hardenability of austenite and the formation of a large amount of martensite, cooling rate after hot rolling or coiling should be set low.
- As an austenite-stabilizing element, Ni works favorably for the formation of retained austenite, and increases the fraction of retained austenite at high CT, thereby improving both tensile strength and elongation.

TRIP-aided cold-rolled sheets, intercritically annealed at 780-790°C and isothermally treated at 430°C were investigated in [48]. The formability (measured with limiting dome height test) as well as the tensile properties of the Cu and Ni-containing cold-rolled steel sheets was greatly improved as the strain-induced transformation of retained austenite was actively sustained up to the high strain region, because of high volume fraction and stability of retained austenite. The cold-rolled steel sheets with Cr added alone or in combination with Ni showed a dual phase structure, together with low-volume fraction and stability of retained austenite resulting from a large amount of transformed martensite. These results indicate that when elements such as Cu, Ni, Cr are positively used, low-carbon TRIP-aided cold-rolled steel sheets having mechanical properties suitable for various application purposes and excellent formability may be achieved.

An ULC steel alloyed with Ni, Mn, Mo and Cu and microalloyed with Mb and Ti was subjected to a three-stage controlled rolling operation followed by water quenching in reference [49], and the effect of thermomechanical processing on the microstructure, mechanical properties, and age-hardening behavior of the steel was evaluated.
The high-strength values obtained are due to the fine-lath martensite structure along with tiny precipitated of microalloying carbide and carbonitride of Ti and Nb at all finish rolling temperatures. The increased strength value at the lower final rolling temperature (FRT) is due to the finer lath width and packet size of martensite. The large TiN and the coarse martensite-austenite constituents impaired the impact-toughness value of the steel at subambiant temperature. At low ageing temperatures, coherent Cu particles form and a peak strength is obtained due to the formation of fine ε-Cu precipitates. On increasing ageing temperature, the Cu particle size increase, decreasing dislocation density in the matrix resulting in a decrease in strength, see Figure 25.

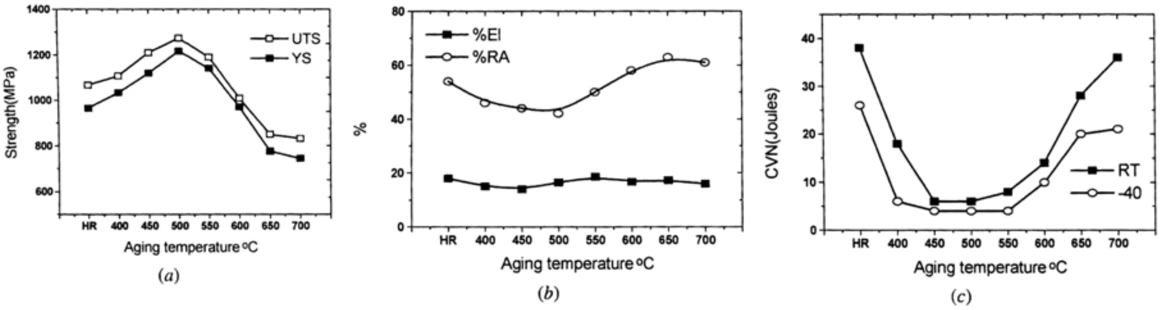


Figure 25 Variation in mechanical properties of the TMCP steels at different FRT. (a) Hardness, UTS and YS. (b) pct elongation and % reduction in area. (c) Impact toughness values at room temperature and at -40°C.

Reference [28] presents a review of Russian studies on the effect of copper on structural steels. Precipitation hardening processes are observed in copper-containing structural steels which are caused by a change of it’s solubility in ferrite depending on temperature: up to 400-600°C the solubility of copper does not change and is 0,2 – 0,4%, the hardening process is noted at 0,5% Cu and more. Weak matrix solid-solution hardening of ferrite is noted in copper-containing steels: each 0,1% Cu increases the yield strength by 3,5 Mpa, whereas due to precipitation hardening – by 24,8 Mpa. The maximum effect is achieved during tempering at 500°C for 4 hours: the hardness HB increases from 145 to 245 in steel with 0.19% C and 1.07% Cu.

Reference [41] presents high strength low alloy (HSLA-100) steels with copper additions, which were developed in order to reduce production costs while simultaneously improving the quality of structural steels. The composition of this steel is given in Table 8 (see previous chapter) The role of copper in contributing to the developments in microstructure and mechanical properties of this steel is summarized as follows:

1. Cu, when in solution in austenite at 900°C, will act to lower the transformation temperature (Ms or Bs) upon quenching. This will lead to an overall increase in strength at all ageing conditions.
2. Cu, when in the form of precipitates, will contribute to the overall strength by precipitation hardening when aged near 450°C.
3. Cu, when in the form of precipitates, will act to retard the recovery and recristallization of the as-quenched matrix. This will also lead to higher strength levels at all ageing conditions.
4. As the ageing temperatures increases, the amount of Cu in the austenite also increases. This acts to lower the Ac_1 and leads to the formation of new austenite at lower ageing temperatures.

The retardation of recovery and recrystallization together with the low temperature formation of stable austenite combine to give the aged structure an excellent combination of strength and low temperature toughness.

Grain boundary embrittlement

Residual elements can induce embrittlement due to garin boundary segregation [16]. Residuals may segregate to the grain boundary during cooling and coiling in the hot strip mill, or during final annealing after cold rolling. An important related aspect is the ability of the elements to reduce grain boundary cohesion, which makes fracture more likely. It was calculated [50] that the grain boundary cohesion in ferrite is reduced in proportion to the excess size of the segregated atoms (see Figure 26 B). Cold embrittlement in steels occurs at the so called transition temperature (TT), at which deformation mode changes from dislocation displacement to grain boundary decohesion. This prevails at lower temperatures. Residuals such as Sn, Sb, As and P increase the TT, whereas Be, C and B decrease it.

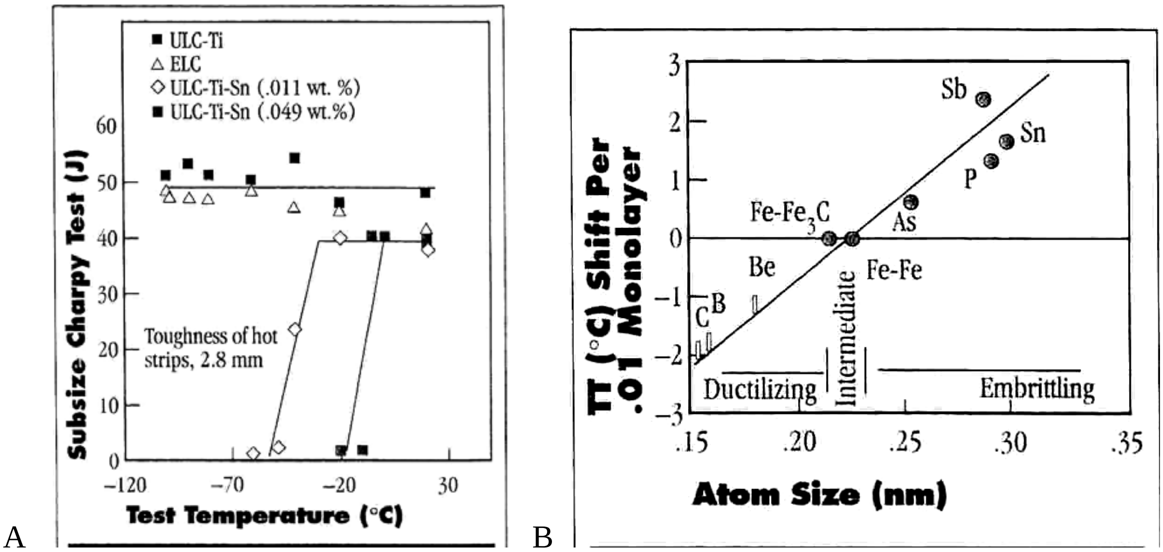


Figure 26 Influence of Sn on the toughness of hot-rolled strips (A). Relation between atom size of residual elements and embrittlement (B).

Sn, Sb, As, Cu, F, P, S, An, Zn, Pb and Bi tend to segregate at surfaces, which reduces the grain cohesion and causes grain boundary embrittlement in steel when they are present in sufficient high concentrations.([7] and [6])

According to reference [16], the thoughness of hot rolled strips is drastically reduced by P due to grain boundary segregation during slow cooling after transformation (medium C steels and vacuum degased IF steels). No remarkable effect caused by Sn, As and Sb were detected in medium C steels. This may be due to the protection by soluble C diffusing to grain boundaries. However, Sn drastically reduces the toughness of hot rolled ULC-IF steel grades (see Figure 26 A). In that case, all C atoms are tied up by Ti or Nb additions.

Corrosion

The segregation of copper to the surface is often considered as a problem due to hot-shortness. It can however present advantages for corrosion resistance, which are useful in weathering steels. This range of alloys is designed to corrode uniformly with the re-precipitation of Cu^{++} at the surface. Cu also has the property of being electroreducible, deposition as Cu^0 and forming complexes with iron at the surface of carbon steels which prevent further corrosion. In even quite aggressive atmospheres, the beneficial effect of Cu (0.2 – 0.4%) is important, see Figure 27. [3]

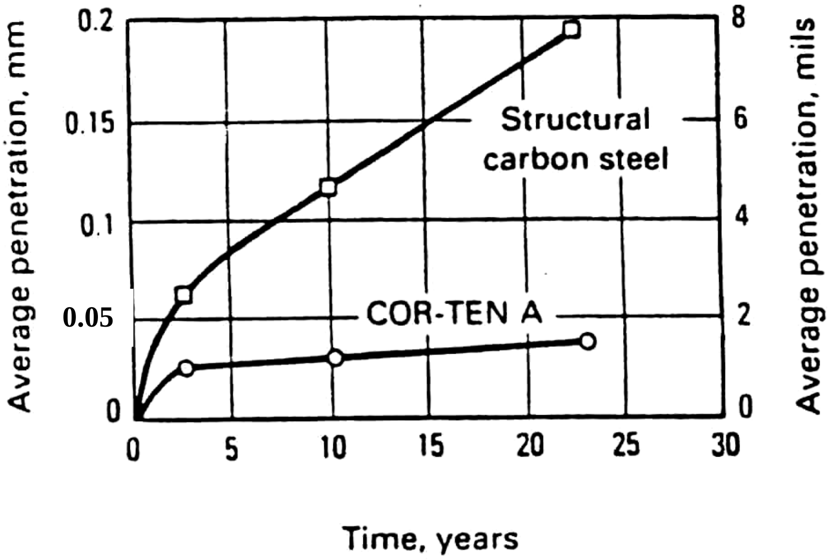


Figure 27 Time/corrosion curves showing relative performance in a semi-industrial environment.

Also according to reference [28], the resistance of steel to atmospheric corrosion increases considerably with copper addition. Losses from corrosion of structural steel decrease almost twofold with increase of copper content from 0,1 to 0,3%.

5.3 Welding

The effects of residual elements on the welding properties of low alloyed steels are widely varied. Most residual elements contribute to the hardenability in the HAZ of a welded material in a more or less negative way. The weldability of a material, as listed in reference [18], can be judged by its properties in relation to:
1. Hot cracks during solidification.
2. Lack of fusion, blowholes and spatter.
3. Cold cracking, hydrogen embrittlement.
4. Lamellar tearing.
5. Weldment strength.
6. HAZ toughness.
7. Weld metal toughness.
8. Loss of toughness during stress relief treatment.
9. Reheat cracking
10. Weldment fatigue strength.
11. Preferred corrosion for example due to formation of Chromium carbides in the grain boundaries, causing chrome or other carbide formers to be leeched from the grain boundaries.

Hot cracking, also called solidification cracking, occurs in the boundary between the weld metal and the base material. When the melted material cools down, grains grow from the material in towards the thermal centre of the weld. The composition of the material in this zone is dependent on both the base- and the weld material, as the part of the base metal is melted along with the weld metal. As the melt solidifies segregation and solidification shrinking occurs. This can cause low melting phases to be present as the material solidifies, which can cause tearing and cracking in the weld.
In different models developed to calculate the so called ‘carbon equivalent’, used to estimate among others the susceptibility to cold cracking, there is a great variation in coefficients for a specific element in the different formulae [51], showing that it is difficult to estimate the effect of any given element.

The effect of copper on the weldability of steel is quantified through its contribution towards the material tendency for hot and cold cracking. Copper has a tendency to cause hot cracking. Usually the hot cracks associated with copper are small but can serve as initiation points for future cracking and stress corrosion cracking. Hot cracking occurs when a critical strain is applied at elevated temperatures. The problem of hot cracking can generally be avoided as long as the applied strain at high temperature remains below the critical value for the given material.

The solubility of copper in austenite is higher than in ferrite; this causes the matrix to become supersaturated with copper as austenite transforms to ferrite during sufficiently high cooling rates. If the cooling rate is slow the copper will form precipitates in the bulk matrix of the steel. The hardening of the material by dispersed fine grains of precipitated copper is one of the reasons for alloying steels with copper. The hardenability of the HAZ is inversely related to the weldability: higher hardenability leads to lower weldability. The finely dispersed precipitates can also contribute to a refinement of the grain size in the HAZ. The refinement of the microstructure contributes to increasing the toughness in the weld. It is not only the copper content of the bulk material that has to be considered

though, but also the copper content of the welding rod that together with the bulk material make up the total copper content in the weld.
Copper by itself seems to have a limited effect on the weldability of C-Mn steels, but in combination with Sn, Sb and As copper has a strongly negative effect. This can partly be attributed to the lowered solubility of copper in austenite when the austenite is containing Sn, Sb and As. It is suspected, but not extensively researched, that the same problem as with hot shortness, i.e. presence of a liquid copper phase, is responsible for the poor welding qualities in this case. It has been observed according to [52] that the addition of copper, from scrap in steels produced through EAF route, does not seem to have any negative effects on either the base material or on the welded metal in the HAZ concerning levels up to 1 w% Cu.

The presence of sulphur is known to have adverse effects on cracking in the heat affected zone (HAZ) of welded materials. However, when the levels of sulphur are too low, problems with hydrogen cracking in C-Mn steels, or improper penetration in specific Cr-Mo-V steels have been reported [53]. The hardenability of the HAZ is increased with lower oxygen lower sulphur steels and it's considered being the cause of the increased risk of hydrogen cracking. Also it can be noted that sulphur act as a surface reactant and decreases the rate at which nitrogen is picked up [54]. Therefore higher nitrogen levels can be found in low sulphur steels. Sulphur has affinity towards manganese but can form FeS in low manganese steels. FeS melts at 988 ^{o}C and act much like copper in that it forms a film in the grain boundaries. This behaviour cause hot-tearing which is seen during solidification of the weld material. The sulphide film causes material separation between the grains as they are cooled and undergo solidification strain.

In welded material tin acts together with antimony and arsenic to change the surface energy of the grains, since they have a tendency towards grain boundary segregation. Tin like boron can affect the wetting angle of a copper liquid and lessen the penetration in to the grain boundaries. This decreases the susceptibility to hot-tearing and hot-shortness. But in contrast tin also lowers the solubility of copper in austenite and lowers the melting point and can thereby be severely detrimental in the case of hot tearing.
The decrease in sulphur and oxygen contents in steel has not been only beneficial. Boron is often present as a residual element in steel but has not existed in an active form in steel that was not intentionally alloyed with boron. Previously boron combined with oxygen and nitrogen to form an inactive state. In combination with more aluminum and titanium in modern steels and lower nitrogen and oxygen contents boron can exist in an active form. Even as low levels as 3-5 ppm can have a significant effect on the hardenability of a material. In relation to the amount for a given hardening effect, boron has a large effect [55].

Nickel in combination with manganese and chromium act to restrict occurrence of a copper liquid by increasing the melting point of the copper phase and increasing solubility of copper in the iron matrix.

6. Conclusion

An overview of the possible effects of residuals elements on down-stream process and end properties of steels, classified by their nature in the steel, was proposed, see Figure 28.

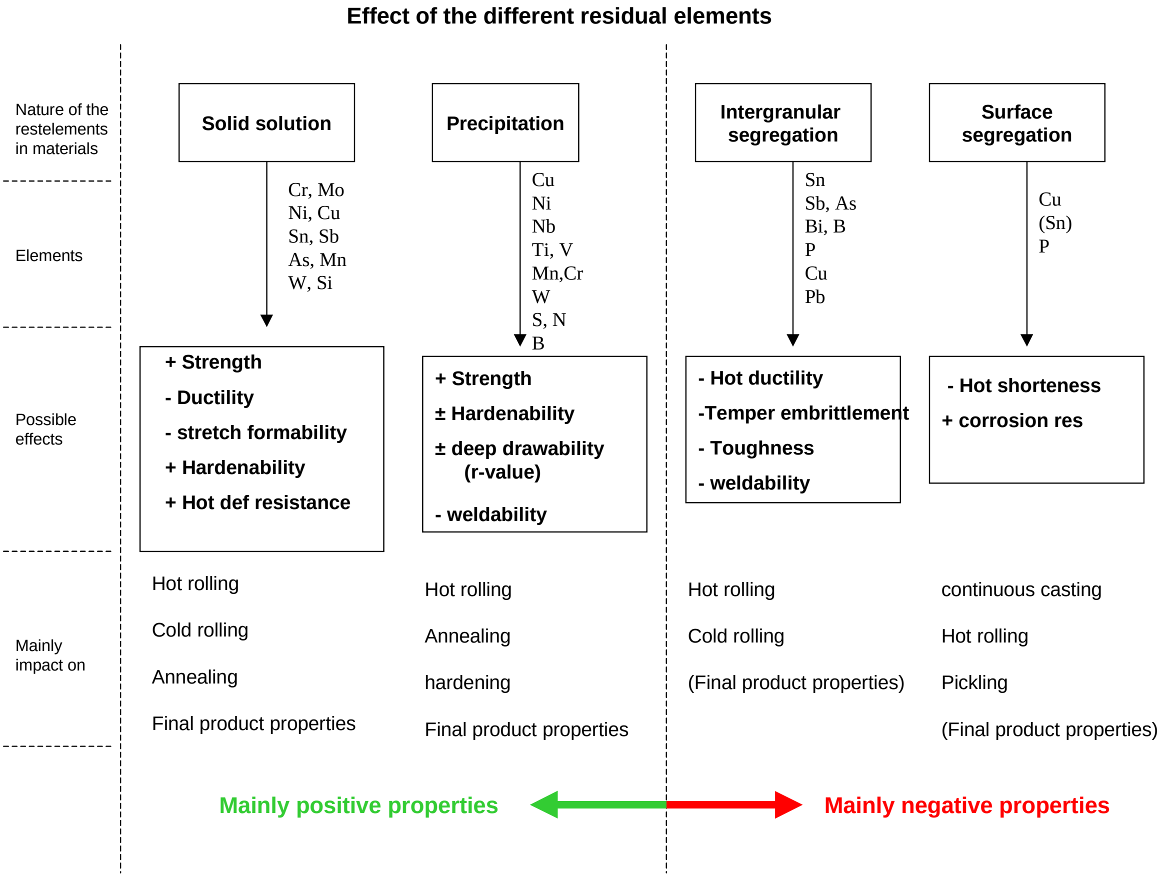


Figure 28 Overview of the nature of residual elements in steels and of their possible effects on down-stream process and end properties.

The effect of residual elements on down-stream process and end properties of low carbon low alloyed steels is a wide topic, which is consequently difficult to briefly summarise. Some general trends and features could however be found, which are presented here. The most remarkable trend is the dominance of Cu in the elements studied: most of the studies are concerned by the influence of copper, alone or in combination with other elements.

Hot working

- Most studies are related to the effect of Cu, which can cause hot-shortness during hot working, even for contents as low as 0.1% in some cases. The critical temperature for hot shortness is between 1100°C and 1200°C. Modifying the process can allow higher Cu contents, at least up to 0.8%.
- Several studies are concerned by the influence of other elements in combination with Cu on hot-shortness, $Cu_{equivalents}$ being presented in some cases. Mainly Sn, but even Mn, Cr, As and V are reported to increase hot-shortness whereas mainly Ni, but even Co, Al and Si are reported to decrease it.
- Grain boundary segregation, which is a non-equilibrium segregation at grain boundaries of mainly Sn, leads to a low hot ductility in the temperature range 600°C to

950°C. Cooling rates between 5 and 20 °C/s were shown to increase risk for grain boundary segregation.

- DSC (direct strip casting) allows higher contents of Cu and Sn in the material without hot-shortness problems, by combining short oxidation time with rapid cooling and direct rolling. Processing windows to avoid hot-shortness were studied at KIMAB.

Cold working

- Elongation and drawability are the main properties used to define cold workability. Residual elements mainly contribute to harden the matrix, which has a negative effect on cold workability. Ni, Cr, Cu, Mo, Sn and As were reported to decrease the ability to deep drawing and formability of LC steels whereas Ti and Nb showed the contrary effect.
- Copper was shown in some cases to have positive effects on formability when processing and heat-treating the material properly.

Hardenability

- Most residual elements, at the exception of Co, Ti and S, increase the hardenability by slowing down the ferrite and pearlite reactions. Mn is reported to be very effective in this purpose, as well as Mo, Cr and P, whereas Ni and Cu are less effective.
- Several studies are concern by copper, which is shown to increase hardenability by decreasing the transformation to ferrite.

End properties

- Most residual elements increase the strength and decrease the ductility, which is mainly due to solid solution hardening and also to precipitation.
- Copper lead to a weak solid solution hardening. However, a high strength was obtained due to the fine dispersion of ε-Cu particles after ageing at low temperatures (450°C to 500°C).
- Cu, Cr and Ni in low C – TRIP aided cold rolled sheets were reported to increase tensile strength and elongation by increasing the content of retained austenite.
- Reduction of the grain boundary cohesion, so called grain boundary embrittlement, is due to the segregation of elements at the grain boundaries during cooling, coiling and final annealing. Sn, Sb, As and P are reported to segregate to surfaces.
- Copper can act as a protection against corrosion in certain steels.

Welding

- Most residual elements contribute to the hardenability in the HAZ in a more or less negative way.
- Steels that contain up to 0.85 w% copper has not reported to be a problem. In fact the forming of precipitates is reported to be beneficial in regards to the toughness of the weldment.
- The combination of tin and copper is a problem both in hot rolling and welding, causing similar problems. The presence of a copper phase that has a low melting point compared to the base material can cause surface cracking during hot rolling and hot tearing during welding as the material solidifies.

7. Summarizing tables, effects of residual elements

The tables presented in this chapter are a summary of observed effects and limit contents of residual elements found in literature.

Table 9 Influence of copper and tin

REF	**Steel type**	**Rest element**	**Critical content (%)**	**Operation**	**Property affected Problem**	**Comment**
6		Cu	0.1		Surface defects	Sb, Sn, As increase problem Ni reduces problem More problems with lower C content
4		Cu	0,2		Hot workability	
3		Cu	0.2		Hot-shorteness	Sn and Sb increase the effect, Ni decrease it. Ni can be problem , adherent scale → surf. Defect → wear of process tool.
3	Engineering steels	Cu	0.35-0.47	Continuous casting	Intergranular cracks in areas under mech. Stress. Problem if hold time at 1100°C	Cracking severity f(casting process) Ni inhibit cracking (same amount as Cu) Solution: strong cooling after mold extraction
3	Low carbon steels	Cu, Sn	0,8 / 0.05	Continuous casting	Intergranular cracks, increase with Cu, Sn%	Cueq = Cu + 8Sn - Ni
3	Engineering steels, low carbon steels	Cu	0.26	Reheating furnace	Cracking if 0.26% Cu and long time	0.14% Cu and long time → less cracking. Two opposite effects.
3	Engineering steels, low carbon steels	Cu	0.4	Hot rolling	Increase ultimate tensile strength, decrease elongation.	Litte influence on the surface quality (cracking).
57	Flat products	Cu, Sn	0.1 + 0.025	Hot forming	Surface cracking	
57	LC steel (o.15% C)	Sn	0.061	Cont-cast, thermal simul tests	Hot ductility decreases (RA value). Lowest value at 750°C, not dependent on Sn content	Grain boundary segreagation during cooling. Maximum segregation for cool.rate between 5 and 20K/s.
57	Deep drawing steel	Cu	0.1	Cold forming / cold drawing	negative	
4		Sn	0,04		Hot workability	
7	ELC, 0.02%C	Sn, As	0,08 *		Static recrystallization delay	Temp 950°C
57	Deep drawing steel	Sn	0.02	cold drawing	Negative, increase yield and tensile strength,	impairs elongation and striction

Table 10 Influence of residuals on processing

REF	Steel type	Rest element	(Critical) content (%)	Operation	Property affected Problem	Comment
4		Zn			Forms white smoke during iron casting	Dust treatment required
4		Pb	0,001		Hot workability	
57		Pb	0.001 – 0.005	Hot forming	negative	
4		As	0,03		Hot workability	
57	LC steel	As	0.03	Hot forming	negative	
4		Bi	0,005		Hot workability	
57		Bi	0.0005	Hot forming	Harmful	
57		S		Hot forming	negative	
16	ELC steels	Mo, Cr	0.09 / 0.09	Hot compression tests	Increase hot def resistance, delay static recristallization	➔ higher rolling load
7	0,03%C	Cr, Ni, Mo			R 90 Decrease drawability	Annealing T 680°C
16	ELC steels	Ni, Cr, Cu, Mo		Cold rolled and annealed sheets	Increase the resistance	Could be a problem for soft drawable steel grades
16	ELC steels ULC-IF steels	Sn, As, Cu, Ni, Cr, Mo			Decrease r-value and ductility ➔ adverse effect on drawability	
57		Cr, Mo, N		cold drawing	negative	
16	ELC steels	As, Sn		annealing	Recrystallization delay for cold rolled steels	Both continuous annealing and batch annealing.
57	LC steels	P	0.03	Cold forming / cold drawing	Negative, increase yield and tensile strength	
57	LC steels	As	0.025	Cold forming / cold drawing	Negative, increase yield and tensile strength	

Table 11 Influence of residuals on end-properties

REF	Steel type	Rest element	(Critical) content (%)	Operation	Property affected Problem	Comment
4	Sheet product	Ni, Cr			Increase hardness	
3		Cr, Mo, Ni, Cu	Solid solution		Increase hardenability of C and low alloy steels	Cr and Mo stronger effect
3		Cr, Cu, Ni, Mo	Solid solution		Increase hardness, decrease ductility	Cr > Cu, Ni, Mo. Cr effects depends on C concentration
3	If-Ti, thin sheet	Cu, Ni, Cr, Sn	Solid solution		Decrease grain size, increase solid solution hardening	
3	Low alloyed steels, high res. martensitic stainless steel	Cu	0.5		Increase hardness	Precipitate during aging treatement in the form of ε-Cu.
57		Sb, P		Hardenability	increase	
57		As	0.045	Hardenability	decrease	
57		B	0.0005	Hardenability	Increase strongly	
57		Cr		Hardenability	Increase moderately, strong carbide former	
57		Mo		Hardenability	Increase strongly, carbide former	
57		Co		Hardenability	decrease	
57		Cu, Ni		Hardenability	Mildly increase	
57		N		Hardenability	decrease	Nitride former, decreases grain size dimension and hardenability.
57		W		Hardenability	Strong increase	
57		S		Hardenability	Decrease by removing manganese from solution	
3	Weathering steels	Cu	0.2-0.4		Resistance to corrosion	Cu at the surface ➔ better corrosion resistance.

Table 12 Influence of residuals on end-properties

REF	**Steel type**	**Rest element**	**(Critical) content (%)**	**Operation**	**Property affected Problem**	**Comment**
16	ULC-IF	Sn (even others)			Reduce drastically toughness of hot rolled steels	Embrittlement due to grain boundary segregation
3	High strength C-Mn steels	P, Sb, Sn	Grain boundary segregation	Tempering slow cooling, service (350 - 550°C	Temper embrittlement	Mn, Cr or Ni necessary to observe the phenomene. Mo can inhibit temper embrittlement if between 0.2-0.7%wt.
57		Sb		Notch impact strength	Promotes temper embrittlement	
57		As	0.045	Notch impact strength	Promotes temper embrittlement, decrease notch impact value	
57	Maraging steel	Pb, P, S	0.005 / 0.01 / 0.014	Notch impact strength	Promotes temper embrittlement, decrease notch impact value	
57		Sn	0.04	Notch impact strength	Promotes temper embrittlement, decrease notch impact value	Effect increase with C content.
7	ULC-Ti hot stripes	Sn	0,011/ 0,049 *		toughness decrease	
10		Cu, As, F, Sn, S, An, Zn, Pb			Grain boundary embrittlement	
3	Thin sheet	Sn			Segregate to grain boundaries	More pronounced with low C.

Table 13 Influence of residual elements on processing and end-properties of flat products, from reference [2]

Product	Steel type	Operation	Residual element	Content	Comment
Flat	Low carbon steel grades	casting	Mo, Cr Nb, Ni	0.05 0.1	OK
		Hot rolling	Sn, Mo, As, Cr		Problem Sn>Mo>As Cr OK
		Cold rolled and annealed sheets	All but not Nb and Ti		Bad for crystallografic textures and r-value. Tensile stress increase at 0.08 (inte så at 0.03)
	ULC, low strength	Hot rolling	Sn, Cu		OK
	ULC, high strength	Hot rolling	Cu Sn	0.3 0.05	Strenght +, elongation – Strenght -, elongation +
			Sn+Cu together		Sn moderates Cu effect
		Cold work			Embrittlement with both Cu and Sn
		weldability			OK with Cu and Sn

Table 14 Influence of residual elements on processing and end-properties of long products, from reference [2]

Product	**Steel type**	**Operation**	**Residual element**	**Content**	**Comment**
Long		Weldability, toughness, service properties	Cu Sn	0.585 0.03	No deterioration
	Heavy plate materials, CMnNb grade	Strength and elongation	Sn	0.02	Slight effect, OK
	42 CrMo4, 34 CrNiMo6, 15 CrNi6	hardenability	Mo Cu		Mo and Cu most important elements for hardenability
	LC steel 20 MnCr5, 7 MB6	Hot ductility	Cu Sn	0.4 0.03	Degradation over these contents. Harmfull effect ceases for T over 1100°C.
		Surface cracking	Cu	0.3	Critical Cu content. Lower if Sn, Sb present, higher if Ni present.
	LC direct quenched wire rods	Cold bright drawing	Cu	0.5	Very good results for Cu>0.5
		Cold bright drawing	Cr, Mo, Ni		No significant effect
	LC free cutting steel, 0.08C, 11Mn, 0.07P, 0.3S + Bi, Te	Cutting force, tool wear, hot ductility	Cu Sn	0.25 0.05	No effect
			Bi, Te		Strong influence on hot ductility
	High tensile pearlitic steel (0.8C, 0.2Si, 0.5Mn)	Segregation	Cu, Sn, P		Sn large tendency to segregate in hot rolled rods
		Mechanical properties	Cu Sn	0.15 0.05	Cu rises slightly tensile strength, no clear effect of Sn
	LC wire	Continuous casting	Cu	0.25	Precipitation of Cu-rich phase at metal/scale interface, oxide penetration in steel , eliminated by oxidation during billet reheating prior to rolling.
		Descaling			No deterioration
		Phosphationg prior to drawing			No significant effect
		Nickel coating			No significant effect

1. References

1 Gartz R, Nylén M, “Miljöaspekter vid produktion, användning och recirkulering av metaller, IM report 3424, 1996.

2. Marique C., ”Tramp elements and steel properties: a progress state of the European project on scrap recycling”, La revue de Métallurgie-CIT pp.433-441, 1998.

3 Houpert C, Jallon M, Confente M, Lanteri V, Jolivet JM, Guttmann M, Birat JP, “Production of high quality steels using the scrap/electric arc furnace route”, 15th PTD conference proceedings, pp.67-77, 1996.

4. Sano N, Hiroyuki K, Sasabe M, Shigeki M, “Research activities on removal of residual elements from steel scrap in Japan”, Scandinavian journal of metallurgy, vol.27, no.1, pp.24-30, 1998.

5 Tsukihashi F, “Thermodynamics of removal of tramp elements from steel scrap”, Met. and mat. Processing, vol. 1, pp.927-936, 2003.

6. Sarov L., Janke D., “Recycling of scrap in steelmaking in view of the tramp element problem”, Metall 52, Nr6, 1998.

7. Nilles PE, “Recycling and virgin materials in the changing European steel industry”, Iron and Steelmaker vol.24, n0.4, pp.33-40, 1997

8 Birat JPL, “Residuals and tramp elements in scrap and steel”, 15th PTD conference proceedings, pp.53-65, 1996.

9 Skrotboken 2000, utgåva 1, revised 2005.

10. Kor GJW, “Residual elements in steelmaking”, 54th electric furnace conference proceedings, pp.477-495, 1997.

11 Menad M, Björkman B, “Tramp elements in Steelmaking, literature survey”, report from Luleå university of technology, April 1998

12 Cho WD, Fan P, Han G, “A new approach for the removal of Copper from solid ferrous scarp”, AIS Tech. Proceedings vol.1, pp 861-867, 2004.

13 Hawkins RJ, “Problem of residuals in Steel- current situation in the ECSC”, Vol.12, no.6, pp.286-287, 1985.

14 Yuuji Kimura, Setsuo Takaki, “Phase Transformation Mechanism of Fe-Cu Alloys”, ISIJ International, Vol. 37 (1997), No. 3, pp. 290-295

---

15 L. G. Garza, C. J. Van Tyne. “Surface hot-shortness of 1045 forging steel with residual copper” Journal of Materials Processing Technology 159 (2005) pp. 169-180.

16 Herman JC, Leroy V, “Influence of residual elements on steel processing and mechanical properties”, Iron and Steelmaker, vol.23, no.12, pp.35-43, 1996.

17 Yamamoto K, Shibata H, Mizoguchi S, “Defective or effective? – tramp elements in steel”, Trans, Indian Inst. Met. Vol.58, no.4, pp.695-702, 2005

18 N.E. Hannerz, “Review on the influence of copper content on weld metal properties”, Welding in the world. Vol. 26, No. 11/12, pp. 326-339, 1988

19 Miras Djurovic, Bosko Perovic, Kata Kovacevic, Amlica Koprivica, Milojica Andjelic, “The effect of residuals on the susceptibility to surface cracking and hot deformability of plain carbon steels” Materials and Technology (Slovenia). Vol. 36, no. 3-4, pp. 107-113. May-Aug. 2002

20 Nylén T, “Influence of Cu, Sn and other residuals on the break-out frequency and amount of surface defects during continuous casting”, IM report 1763, 1982.

21 Othani H, Suda H, Ishida K, “Solid/Liquid equilibria in Fe-Cu based ternary systems”, ISIJ International, vol.37, No.3, pp.207-216, 1997.

22 Technical steel research report, “Effects of tramp elements in flat and long products” EUR 16672, ISSN 1018-5593.

23 Imai N, Komatsubara N, Kunishiga K, “Effect of Cu, Sn and Ni on hot workability of Hot-rolled mild steel”, ISIJ International, vol.37, No.3, pp.217-223, 1997.

24 Imai N, Komatsubara N, Kunishiga K, “Effect of Cu and Ni on hot workability of Hot-rolled mild steel”, ISIJ International, vol.37, No.3, pp.224-231, 1997.

25 Nagasaki C, Kaga M, Shibata K, Asakura K, and Hatano M. “Effect of Boron on Copper Induced Surface Hot Shortness of 0.1% Carbon Steel” ISIJ International, Vol. 42 (2002), Supplement, pp. S57-S61.

26 Seo S-J, Asakura K, Shibata K, “Effects of 0.4%Si and 0.02%P additions on surface hot shorteness in 0.1%C-0.5%Mn steels containing 0.5%Cu”, ISIJ International, vol.37, No.3, pp.240-249, 1997.

27 Hideki Ono-Nakazato, Kenji Taguchi, Yutaka Seike, Tateo Usui, “Effect of Silicon and Carbon on the Evaporation Rate of Copper in Molten Iron, ISIJ International, Vol. 43 (2003), No. 11, pp. 1691-1697.

28 Mininzon RD, Potapov VD, Spektor YM, Moshkevich EI, Nikitin SB, “Investigation of the effect of high copper content on the properties of steels 20 and 40Kh”, Steel in Translation, vol.30, No.12, pp.64-69, 2000.

---

29 Shibata K, Seo S. J., Kaga M, Uchino H, Sasanuma A, Asakura K, Nagasaki C, “Suppression of Surface Hot Shortness due to Cu in Recycled Steels” *Materials Transactions,* Vol. 43, No. 3 (2002) pp. 292-300.

30 Yuan ZX, Jia J, Guo AM, Shen DD, Song SH, Liu J, “Influence of tin on the hot ductility of a low-carbon steel”, Acta metallurgica sinica, vol.16, no.6, pp.478-482, 2003.

31 Matsuoka H, Osawa K, Ono M, Ohmura M, “Influence of Cu and Sn on hot ductility of steels with various C content”, ISIJ International, vol.37, No.3, pp.255-262, 1997.

32 Spitzer KH, Ruppel F, Viscorova R, Scholz R, Kroos J, Flaxa V, “Direct Strip Casting (DSC) – an option for the production of new steel grades”, steel research 74,no.11-12, pp.724-731, 2003.

33 Liu Z, Kobayashi Y, Nagai K, “Effect of nanoscale copper sulfide particles on the yield strength and work hardening ability in strip casting low carbon steel”, Material transactions, vol.45, no.2, pp.479-487, 2004.

34 Eliasson J, Siwecki T, Hutchinson B, “Processing and final properties of strip cast steel products containing copper and tin from scrap”, IM-2003-134 report, 2003

35 Kameno K, Nomura S, Kokubo I, “Copper bearing high strength cold rolled steel sheets with superior drawability”, SAE Technical Paper Series 820022, 1982.

36 Ohmori A, Matsuzaki A, Amano K, “Effect of Cu, Sn and Sb on Cold forgeability of a 0.5% carbon steel”, ISIJ International, vol.47, No.3, pp.302-304, 1997.

37 A.K. Roy, S.K. Bhattacharyya, G. Krauss, “The Effect of Sulphur and Niobium on Machinability of Micro-Alloyed Steels”, Key Engineering Materials Vol. 84-85 (1993) pp. 308-330.

38 ASM Handbook online: “http://products.asminternational.org.

39 Desalos Y, Laurent R, Thivellier D, Rousseau D, “Influence of tramp elements on hardenability and cold ductility of carbon and carbon-manganese steels”, Revue de metallurgie, vol.77, no.12, pp.1011-1025, 1980

40 Kasuya T, Ichiwa K, Fuji M, “Derivation of carbon equivalent to assess hardenability of steel”, Science and Technology of Welding and Joining, voö.3, no.6, pp.317-320, 1996.

41 Mujahid M, Lis K, Garcia C, DeArdo A, “Structure – Properties studies of Cu containing HSAL-100 Steels”, Proceedings of the International Conference on Processing, Microstructure and Properties of Microalloyed and High Strength Low Alloy Steels, pp. 345-357, 1991.

42 Malyshevskii V, Semicheva T, Khlusova E, “ Effect of Alloying Elements and Structure on the properties of Low-Carbon Heat-Treatable Steel”, Metal Science and Heat Treatment, vol.43, no. 9-10, pp. 331-335, 2001.

43 Ohtsuka H, Ghosh G, Nagai K, “Effects of Cu on diffusional transformation behaviour and microstructure in Fe-Mn-Si-C steels”, ISIJ International, vol.37, No.3, pp.296-301, 1997.

44 Kimura Y, Takaki S, “Phase transformation mechanism of Fe-Cu alloys”, ISIJ International, vol.37, No.3, pp.290-295, 1997.

45 T. Yamada, M. Oda, O. Akisue, “Effects of copper, nickel, chromium and tin on mechanical properties of titanium-bearing extra low-carbon steel sheets” ISIJ International, Vol. 35 (1995), No. 11, pp. 1422-1429.

46 Xu S., Brown J.R., Tyson W.R, “Influence of residual elements on mechanical properties of two carbon steel grades”, CANMET, not published yet.

47 Kim S, Lee C, Lee TH, OH C-S, “Effects of tramp elements on Formability of Low-carbon TRIP-aided multiphase cold-rolled steel sheets”, ISIJ International, vol.44, No.4, pp.737-743, 2004.

48 Kim S, Lee C, Lee TH, Lee S, “Effects of coiling temperature on microstructure and mechanical properties of high-strength hot-rolled steel plates containing Cu, Cr, Ni”, ISIJ International, vol.40, No.7, pp.692-698, 2000.

49 Ghosh A, Mishra B, Chatterjee S, “Microstructure, properties and age-hardening behaviour of a thermo mechanically processed ultra low-carbon Cu-bearing High-Strength Steel”, Met. and Mat. transactions, Vol 36A, pp.703-713, 2005.

50 Seah MP, “Mechanisms of Adverse effects (of tramp elements)”, Ironmaking Steelmaking. Vol.12, no.6, pp.288-289, 1985.

51 Technical steel research report, “Effects of tramp elements in flat and long products” EUR 16672, ISSN 1018-5593

52 G. Axmann, R. Creutz “Influence of Tramp Elements on the Mechanical Properties and the Weldability of Structural Steels” EUR 19468 – Primary steelmaking, Recycling of scrap for high-quality products 2001. ISBN 92-894-1098-1 pp.85-95

53 A.J.M. van Deudekom, “The influence of residual elements in Cr-Mo-V low alloy steel (1.7734) on arc behaviour during TIG welding” DVS Berichte, no.154. Welding in Aerospace Industry, Proceedings, 3rd International Conference, Essen; 21-22 Sept. 1993. pp. 40-43. 1993.

54 J Malcolm Gray, William J Fazackerley, “The use of electric arc furnace and thin slab cast steels and their effects on welded construction” WTIA/APIA/CRC-WS International conference Weld metal hydrogen cracking in pipeline girth welds, Wollongong, March 1999.

55 P Hart “Effects of steel inclusions and residual elements on weldability” Metal Construction October 1986 pp. 610-616.

---

56 Carlsson G, “Future trends and Technology forecasts in refining – a European view”, 6th international conference in refining process, pp.19-50, 1992

57 Vallomy JA, “Adverse effects of tramp elements on steel processing and products”, Industrial Heating Vol.52, no.6, pp.34-38, 1985.

THE SWEDISH STEEL PRODUCERS' ASSOCIATION

Since its foundation back in 1747, Jernkontoret has been owned jointly by the Swedish steel companies. Jernkontoret represents Sweden's steel industry on issues that relate to trade policy, research and education, standardisation, energy and the environment as well as taxes and levies.

Jernkontoret also manages the joint Nordic research in the steel industry.

In addition, Jernkontoret draws up statistical information relating to the industry and carries on research into the history of mining and metallurgy.

JERNKONTORET
Box 1721, SE-111 87 Stockholm, Sweden   Kungsträdgårdsgatan 10
Telephone +46 8 679 17 00   Fax +46 8 611 20 89
E-mail office@jernkontoret.se   www.jernkontoret.se