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EFFECT OF TRACE AND RESIDUAL ELEMENTS ON THE HOT BRITTLENESS, HOT SHORTNESS AND PROPERTIES OF 0.15–0.3 % C Al-KILLED STEELS WITH A SOLIDIFICATION MICROSTRUCTURE

UČINEK ELEMENTOV V SLEDOVIH IN PREOSTALIH ELEMENTOV NA KRHKOST IN POKLJIVOST V VROČEM JEKLA Z 0,15 – 0,3 % C, POMIRJENEGA Z Al IN S STRJEVALNO MIKROSTRUKTURO

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The formation of cracks in steels with a solidification microstructure is connected with either the precipitation and segregation of residual elements during solidification and/or with the accumulation of some residual elements at the scale–metal interface during the soaking of the blocks. Hot-brittleness is connected with the change in the solubility of the trace elements in the solid solution of austenite, with segregations of the surface-active elements to the grain boundaries, with the precipitation of small particles at the grain boundaries during solidification and cooling to the hot working temperature, and with the effect of some elements on the solidification microstructure. In this article an overview of the hot brittleness of steels cast in the peritectic range is presented.

Key words: solidification, hot-brittleness, hot-shortness, segregation, precipitation, residuals, selective oxidation, grain-boundary penetration, hot-cracks

Nastanek razpok v jeklih s strjevalno mikrostrukturo ima dva vzroka: izločanje in izcejanje elementov v sledovih med strjevanjem/ali bogatenjem vsebnosti nekaterih oligoelementov na meji škaja-kovina med ogrevanjem blokov. Vroča krhkost je povezana s spreminjanjem topnosti oligoelementov v trdni raztopini v avstenitu, z izcejanjem površinsko aktivnih elementov po mejah zrn, z izločanjem drobnih delcev po mejah zrn med strjevanjem in ohlajanjem na temperaturo vroče predelave ter z učinkom nekaterih elementov na strjevalno mikrostrukturo. V tem članku je prikazan pregled vroče krhkosti litega jekla v območju peritektika.

Ključne besede: strjevanje, krhkost v vročem, pokljivost v vročem, izcejanje, izločanje, oligoelementi, selektivna oksidacija, penetracija po mejah zrn, razpoke v vročem

1 INTRODUCTION

The increasing use of steel scrap in electric arc furnaces means a constant increase in the quantity of residual elements in steels. These residual elements (Cu, Ni, As, Pb, Sn, Sb, Mo, Cr, etc.) are defined as elements that are not added to steel and which cannot be removed by current metallurgical processes. The effect of some residual elements is connected with their presence in the solid solution, such as Mo, Cr, Ni, and Cu, while others segregate at the interfaces (surfaces and grain boundaries), such as Sn, As, and Sb[1], and some effect the solidification microstructure, as Al and N. Some of these elements can be removed by appropriate processing, while some cannot be removed from the molten steel and induce hot brittleness and hot shortness in the steels. The brittleness is found mostly for steel with carbon in the peritectic range of 0.07 % to 0.18 % C. During the solidification of steel the trace elements and other impurities concentrate in the last melt and are pushed by the solidification front towards the interdendritic regions. There they may facilitate the formation of cracks or cause brittleness of the steel when the steel is exposed to shrinkage stress. Some of the residual elements also influence the solidification mode, while some impurities remain in solid solution during rapid solidification and can precipitate from an oversaturated solid solution on the grain boundaries during the cooling of steel after hot working or heat treatment and induce the hot brittleness.

Manganese, aluminium and carbon influence the interparticle distance and the size of the sulphide particles that occur in steel during cooling from the temperature of solidification. An increasing content of manganese increases the size and the interparticle distances, which are lower in steels containing aluminium. It seems that sulphur originates from the segregation during solidification (**Figure 1**), but to draw a conclusion about where the intercrystalline sulphide really originates from is not yet possible[2,3].

The increasing aluminium content promotes a columnar solidification structure in steel. In steel with high aluminium content, coarse columnar grains at the surface of the billets facilitate the propagation of

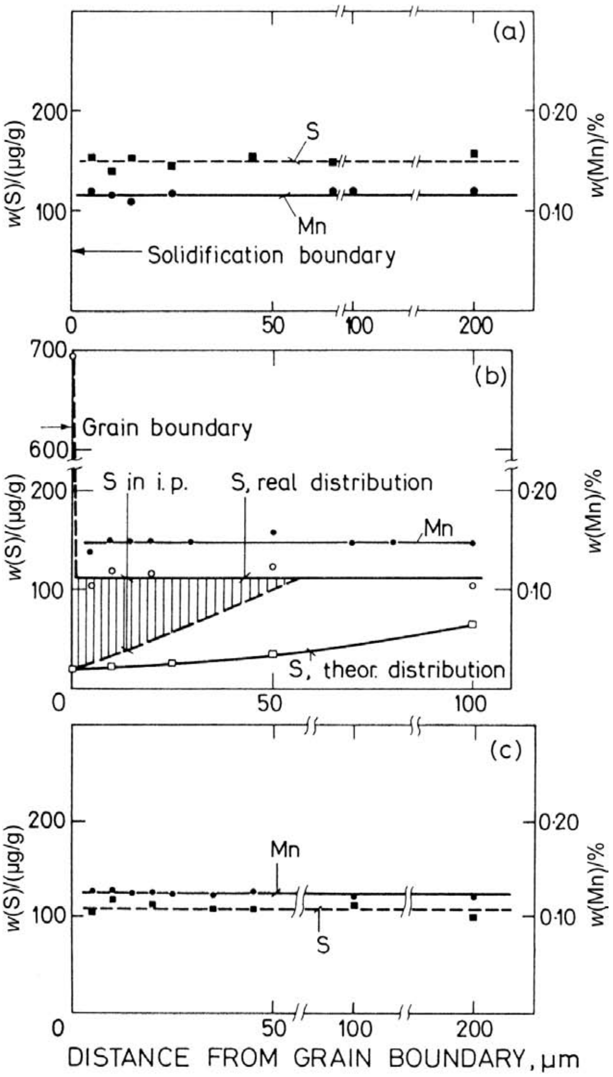

Figure 1: Distribution of S and Mn near the solidification boundary. a) 0.15 % C, 0.18 % Si, 0.33 % S (in mass fractions), specimen cast, stripped and quenched; b) 0.17 % C, 0.20 % Si, 0.14 % Mn, 0.022 % S (in mass fractions), specimen cast, stripped, held for 30 min at 1250 °C and quenched, i. p. is an intergranular precipitate; c) 0.17 % C, 0.02 % Si, 0.022 % S (in mass fractions), specimen cast, stripped, held for 8 h at 1250 °C and quenched[3]

Slika 1: Razporeditev S in Mn blizu strjevalne meje: a) 0,15 % C, 0,18 % Si, 0,33 % S (mas. deleži), vzorec ulit, izvlečen in ohlajen v vodi; b) 0,17 % C, 0,20 % Si, 0,14 % Mn, 0,022 % S (mas. deleži), vzorec ulit, izvlečen, zadržan 30 min na 1250 °C in ohlajen v vodi; i. p. so interkristalni izločki; c) 0,17 % C, 0,02 % Si, 0,022 % S (mas. deleži), vzorec ulit, izvlečen, zadržan 8 h na 1250 °C in ohlajen v vodi[3]

intergranular cracks in length and depth (**Figure 2**). After cooling to ambient temperature and reheating, the structure was identical at all levels of aluminium content and consisted of regular polygonal grains of smaller size. The effect of aluminium should be attributed to a process or a reaction connected with homogeneous nucleation at the start of the solidification[3]. The hot shortness of steels with carbon in the peritectic range is observed mostly in steels with a high content of nitrogen and refined in an electrical arc furnace. This suggests a synergistic effect of aluminium and nitrogen on the solidification structure[4]. With the addition of aluminium the undercooling of the liquid steel is decreased. This reduces the possibility of the formation of a sufficient globular-grains layer near the surface of the billet. If a stronger nitride-forming element, such as titanium, is introduced into the steel, the hot shortness is greatly decreased by an equal content of aluminium and nitrogen. Besides that, every process which modifies the solidification structure of the steel, e.g., recrystallisation and the transformation of austenite, improves the workability of the steel to a

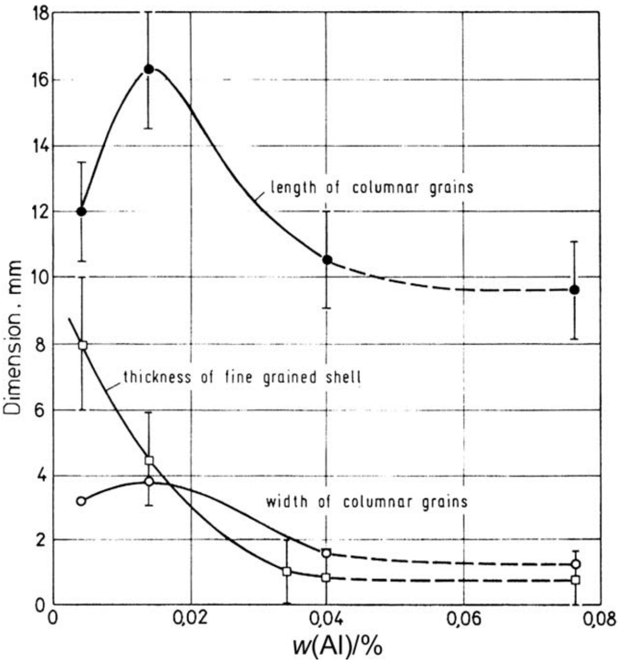

Figure 2: Influence of Al content on the thickness of the equiaxed shell and the length and width of the columnar grains[4]

Slika 2: Vpliv vsebnosti Al na debelino plasti enakoosnih zrn ter dolžino in širino stebrastih zrn[4]

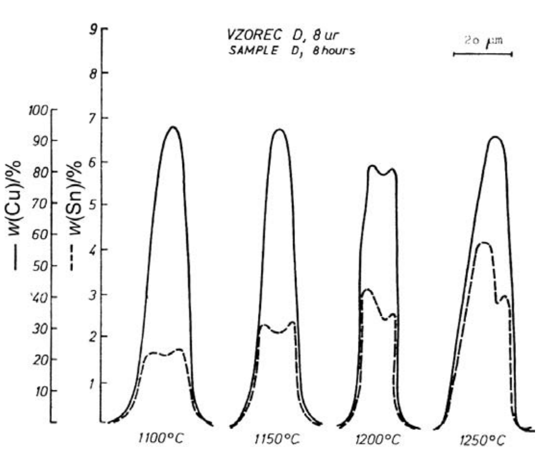

Figure 3: Concentration of copper and tin at the scale–metal interface at various annealing temperatures. Steel contains 1 % Cu and 0.030 % Sn[5].

Slika 3: Koncentracija bakra in kositra na prehodu iz škaje v kovino pri različnih temperaturah žarjenja. Jeklo ima 1 % Cu in 0,030 % Sn[5]

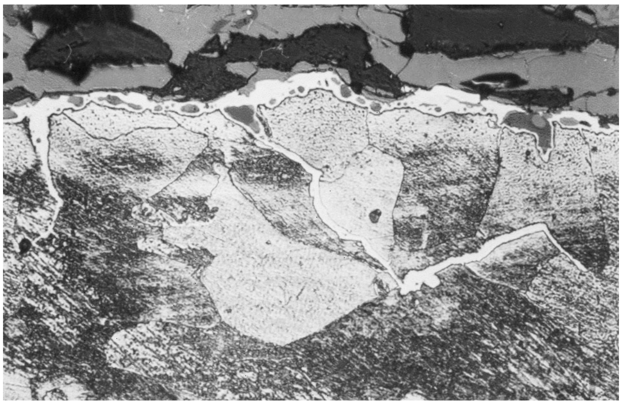

Figure 4: Concentration of Cu-rich phase below the scale after 4 h of annealing at 1050 °C. Etched with Dickenson reagent[6].

Slika 4: Zbiranje s Cu bogate faze pod škajo med 4-urnim ogrevanjem pri 1050 °C. Jedkano z Dickenson jedkalom[6].

great extent and a surface free of rolling defects is obtained on the hot-rolled products.

Hot-shortness occurs during the hot working of steel. Because of selective oxidation, Cu, Sn and other trace elements concentrate in the solid and liquid state at the scale–metal[5] interface (**Figure 3**). Penetration with grain-boundary diffusion along the grain boundaries (**Figure 4**) weakens the cohesion of the grains and induces surface cracks during the hot working[6].

The general influences of residuals on the properties of steel are given in **Table 1**.

Table 1: Effects of the increase in the amount of residual elements on various properties of steel[1]

Property	Cu	Ni	Cr	Mo	Sn	Sb
Strength and hardness	+	+	+,–	+	+	+
Ductility	–	+,–	+,–	–	–	
Strain hardening, *n*	–	–	–	–	–	
Strain ratio, *r*	+,–		–			
Impact resistance	+	+		–	–	
Hardenability	+	+	+		+	+
Weldability	–	–	–	–		
Corrosion resistance	+	+	+		+	
Temper embrittlement					+	+
Elongation	–		–	–		

(+) increase of, (–) decrease of

A large proportion of modern steel production is based on the recycling of steel scrap and the use of only an electric arc furnace (EAF) as a melting aggregate. All the other processing occurs in separate ladle furnaces as secondary or vacuum metallurgy with alloying, rafination and achieving the proper casting temperature. Advances in technology make it possible to remove the sulphur and phosphorus from the steel much more effectively than in the past. But the increased use of scrap in an EAF increases the content of residuals like copper and tin in the steel and causes problems with the hot shortness and hot brittleness of the steels. For this reason, the proper selection of the scrap is of great importance.

The problems with the hot brittleness of steel were intensively investigated in previous years. Numerous studies and investigations have been performed since the early 1900s, when steel's propensity for hot cracking was referred to as red-shortness.

The cause of more intensive investigations in the late 1950s and 1960s was the increase in the amount of steel production from scrap that caused a larger amount of copper and other residuals in the steels[7] and again in the late 1990s, for economic and environmental reasons[8]. The beneficial effect of nickel on the reduction of the detrimental effect of copper was recognized early. Hot brittleness and hot shortness are still encountered and attract more intensive investigations from time to time.

In this article the present state of knowledge with regard to both phenomena is presented.

2 HOT BRITTLENESS OF AS-SOLIDIFIED STEEL

The introduction of microprobe analyses (MPA) in the late 1960s and 1970s produced new knowledge on the hot- brittleness and hot-shortness of steel. The goal of the investigations was to find a mechanism for these phenomena. The intensive study of the solidification processes was performed for the influence of aluminium on the initial deformability of continuously cast C-Mn-Si-N steel[4] and revealed that aluminium influences the hot workability via its influence on the solidification structure. Besides that, the influence of manganese, carbon and aluminium on sulphur solubility during solidification was determined by direct microprobe analysis. As no gradient of sulphur was found in the grain-boundary areas, it was concluded that intergranular particles of MnS do not originate from sulphur in solid solution in the interior of the solidification grains but from grain-boundary segregation during solidification[3]. The intergranular brittleness due to sulphide precipitates causes a severe hot shortness of as-cast 0.16 % C steel with increased contents of aluminium and nitrogen cooled from solidification to the rolling temperature[9].

Sulphide precipitates are one of the reasons for the hot brittleness of steel with an as-solidified structure and hot worked at a temperature below the austenite transformation[9]. An increasing content of manganese increases the size and interparticle distances, which are lower in steels containing aluminium[10,11,12].

Based on the results of investigations and on reference data, two hypotheses are consistent with the data in the references and with the findings of investigation as to why the increased aluminium content reduces the susceptibility of steel to form equiaxed crystals in a layer at the surface and in the core of the billets. One suggests that aluminium widens the region

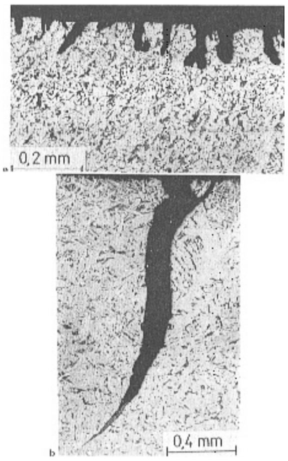

Figure 5: Longitudinal section of cracks at the bent edge of a billet cut. a) shallow non-propagating cracks with blunted tip (0.004 % Al), b) crack propagates to much greater depth (0.04 % Al)[4].

Slika 5: Vzdolžni prerez razpok na upognjenem robu odreza gredice: a) plitve razpoke z zaobljenim vrhom, ki ne napredujejo (0,004 % Al), b) razpoka, ki je napredovala mnogo globlje (0,04 % Al)[4].

of existence of δ-ferrite and the second one suggests the formation of associations of aluminium and nitrogen atoms in the melt, decreasing the undercooling of the melt, which decreases the thickness of the surface layer of equiaxed small grains and exposes the coarse columnar grains to deformation with boundaries perpendicular to the direction of steel deformation.

The hypothesis that hot brittleness is associated with the influence of aluminium and nitrogen on the formation and thickness of a globular layer at the surface of steel, cooled from solidification to the rolling temperature,[13] was confirmed with industrial rolling tests of billets from the same charge but with different contents of Al (**Figure 5 and 6**).

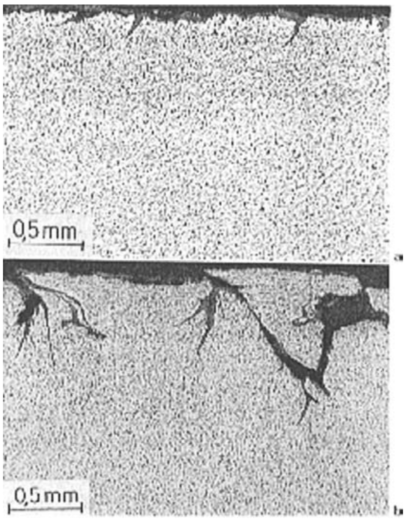

Figure 6: Defects on transverse section of (26 × 70) mm bar rolled in solidification heat. a) 0.004 % Al, b) 0.04 % Al[4].

Slika 6: Napake na prečnem prerezu valjane palice prereza (26 × 70) mm, ki je bila izvaljana takoj po strjevanju: a) 0,004 % Al, b) 0,04 % Al[4].

Many elements segregate to the surface or to the grain boundaries[14,15], like C, Si, N, S, P, Sn, As, with them all being in competition. Tin segregates at the MnS particles and retards the growth of the MnS particles. This has been observed in Fe-3 % Si electrical steel grades[16].

The main reasons for the hot brittleness of steel with an as-cast structure are the effects of elements on the solidification structure and the segregation of surface-active elements or the precipitation of particles on grain boundaries.

3 HOT SHORTNESS OF SOAKED STEEL BLOCKS

It is agreed that the behaviour of copper and tin during the reheating for the hot working of steel is the main reason for the appearance of hot shortness. It was established[17] that tin in the absence of copper is not detrimental to surface cracks. Antimony is likely to be nearly as detrimental as tin because it reduces the solubility of copper in austenite[18].

The most investigated was the effect of copper and of its diffusion. Several studies have shown that at high temperatures the diffusion of copper along grain boundaries prevailed over volume diffusion. Also, more detailed data on the time-dependency of the solubility of copper in steel were established and the conclusion was that the effect of copper diffusivity depended on the temperature.[19,20,21,22,23]

Hot shortness and the resulting increased propensity for cracking are commonly associated with the presence of liquid copper and/or copper-enriched phases at the scale–metal interface.[24,25]

Two stages are involved in the phenomenon: the formation of copper-rich inserts and the penetration along the grain boundaries during reheating and the crack formation during hot working. The scaling rate (temperature, time, and atmosphere) and the deformation temperature are of prime importance for this phenomenon. A complete issue of ISIJ International 37 (1997) 3 is dedicated to the copper-iron system and to trials of the processing modification for the lowering of hot-shortness sensitivity.

Intensive studies of the metallic compounds in the scale layer, below the scale and in the metal[26,27,28] identified the phases known from the appropriate ternary phase diagrams. The beneficial influence of nickel, found in earlier investigations[29], was re-evaluated. It was established that to prevent hot-shortness, the content of nickel should be half that of the copper content. The beneficial effect of the soaking temperature range 1200–1300 °C, with or without the presence of nickel, was also reconfirmed. The main reason for the absence of cracks in this high-temperature region is the rapid diffusion of the copper in the austenite. The diffusivity of copper in iron is five times higher at 1200 °C than at

1100 °C. The consequence of this increased diffusivity is that despite the much higher oxidation rate at 1200 °C than at 1100 °C, the amount of copper-enriched phase at the steel–scale interface was smaller at 1200 °C, compared with that at 1100 °C.

Several studies have focused on the influence of copper and tin on the hot ductility in steels [26,27,28,29,30]. Hot-shortness cracks develop because of surface tensile stresses and boundaries weakened by the grain-boundary copper penetration. The experiments confirmed that the critical temperature of 1100 °C was just above the melting point of copper and that the temperature of 1200 °C was above the reported critical hot-shortness temperature[27,28,31,32,33,34,40]. Above 1100 °C the copper-rich phase is in the molten state at the scale–metal interface. More critical are the lower temperatures when the diffusion of copper along the grain boundaries prevails. The enrichment process is balanced by the dispersion of copper below the scale and the diffusion of copper in iron[26]. Thus, there are two competing mechanisms, grain-boundary penetration and matrix diffusion. The steel's hot-working temperature when the hot-shortness cracks appear, is the breaking point of these two mechanisms.

Copper enrichment at the scale–metal interface occurs due to the selective oxidation of the steel surface and because copper is insoluble in the scale. The oxidation process is a parabolic function of time, and numerous experiments confirmed that the enrichment of copper below the scale depends on the extent of the scaling. The oxidation rate of the steel's surface is temperature dependent, and for this reason the enrichment rate is both temperature dependent and dependent on the content of copper in the steel. For a given temperature, the higher the content of copper in the steel, the higher will be the enrichment. As the temperature increases, both the oxidation and the enrichment rate increase also. At first, the grain-boundary penetration predominates up to the point where the diffusion coefficient of the copper is sufficiently high to start with a planar diffusion front. The diffusion coefficient increases exponentially with temperature. Thus, the enrichment, the dispersion and the grain-boundary penetration are interconnected mechanisms with a temperature window of hot-shortness. The grain-boundary penetration is a diffusion process and it is dependent on the enrichment itself and on the temperature. Without a sufficient amount of copper accumulation below the scale, there is also no significant copper concentration at the boundaries and no problems occur with hot-shortness.

For a high copper content the effect of nickel in steel was investigated. It was found that the addition of nickel to the steel prevented or decreased the hot-shortness for steel with a high copper content (**Figure 7**). The recommended addition of nickel was the same as the content of copper. However, new experiments[27,28] showed that the content of nickel is half the copper content in the steel to prevent the hot-shortness. Other investigations[8,41] showed that in the case of a value of Cu:Ni ratio close to 4, the solidus line from the copper–nickel binary phase diagram was approximately 1160 °C. Nickel increases the Cu-solubility in the austenite as well as favouring the occlusion of Cu in the scale. The effect of nickel results in the modification of the chemical composition of the phases, with a higher melting temperature, formed on the steel surface[24,26,35,36] that lower the propensity for hot cracks' formation.

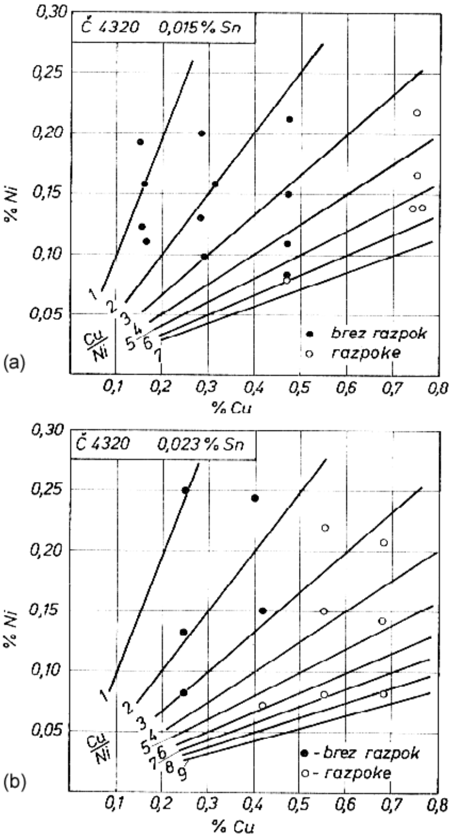

Figure 7: Propensity to hot shortness during a hot-bend test of as-cast steel Č 4320, dependent on the Cu:Ni ratio and the Sn content. a) 0.015 % Sn, b) 0.023 % Sn[41]

Slika 7: Vroča krhkost pri vročem upogibnem preizkusu litega jekla Č 4320 v odvisnosti od razmerja Cu/Ni in vsebnosti Sn: a) 0,015 % Sn, b) 0,023 % Sn[41]

The copper content varies among steels and accordingly variations in the enrichment rate occur. The variation in temperature affects the diffusivity of the copper in the steel, and thus affects its dispersion rate. For steels with a significant copper content, there are two critical oxidation times: the first occurs soon after the formation of the oxide layer, due to copper enrichment from the oxidised steel, and rapid copper penetration into the grain boundaries, that weakens their coherence. By increasing the temperature the scale becomes thicker, the oxidation rate is decreased, while the bulk diffusion of copper is faster and the surface of the steel is less sensitive to cracking. This explains why the steel with copper behaves better at 1200 °C than at 1100 °C in terms of hot cracking. Also, a low temperature and a smaller amount of copper available delay the penetration into the grain boundaries. These two effects explain the maximum cracking being delayed to longer oxidation times.

Several tests were performed[8] to evaluate the newer processing conditions used in modern forge shops that might allow the use of higher copper contents for forging without fear of major surface cracking. A short induction heating time to a temperature of 1200 °C reduces the problems with selective oxidation and the hot-shortness of steel. The forgeability of such steel is similar to steel with a very low copper content.

Besides the residual content of copper in the steel, sometimes copper is added to the steel because of the beneficial influence on some specific properties of the steel. What is well known is that the addition of copper to structural steel increases its atmospheric corrosion properties (in Corten steel, by up to 0.50 % Cu). The addition of Cu is also known to contribute moderately to austenite hardenability[37]. During hot working, in addition to micro-alloying, Cu (mass fraction >0.8 %) contributes to the retardation of recrystallisation and is usually added in a larger amount to achieve the expansion of the unrecrystallised region by the solute-drag effect[35]. A Cu addition also improves the bainitic hardenability and, in the presence of a suitable microalloying addition like Ti or B, bainite may form even under air-cooling conditions[38]. Although the addition of Cu does not effectively contribute to the lowering of the austenite transformation temperature; its addition suppresses the pearlitic transformation by stabilising the austenite at the grain boundaries and triple points of ferrite grains[37].

It was established that the Cu-rich phase is distributed homogeneously in the martensitic matrix of a cutting tool[36–39]. The copper precipitates from the solid solution in ferrite without a uniform orientation and copper precipitates with a size is of approximately 10 nm are formed. These Cu-rich precipitates have a lubricating effect on the contact between the steel and the cutting tool and promote the outflow of the cutting heat. The effect of the lubricant and heat conductivity reduces the cutting-tool wear, improves the machinability and increases the service life of the cutting tool[39].

However, in the exploitation of the beneficial effect of copper on the steel's properties it is necessary to consider the eventual effect of hot shortness. Thus, special care is demanded during the reheating process and the hot working of steels with an increased copper content.

4 CONCLUSIONS

The motivation for all the investigations of hot brittleness and hot shortness is the need to find a solution for the hot working of steels with a high residual-elements content without surface cracking.

It is clear that the content of residual elements in steel will increase with time due to the increasing quantity of scrap recycling. Therefore, it is necessary to identify and to quantify any deleterious effects in order to keep these effects within acceptable limits.

The hot brittleness of as-solidified steel is a consequence of the influence of aluminium and nitrogen on the solidification structure, the presence of the segregations of surface-active elements and the presence of MnS particles at the grain boundaries and residuals' enrichment at the scale–steel surface.

Residual elements, or at least some of them, may affect the processing conditions, and the mechanical properties of the end product. These residual elements are more detrimental in all applications that require low-carbon clean steels, extra-low-carbon clean steel, ultra-low-carbon–interstitials-free clean steel (ELC, LC, ULC-IF) than for the medium- and high-carbon-alloyed steels.

Due to the influence of residual elements and impurities on the hot-brittleness, hot-shortness and on other properties of steels, plants using recycled scrap for steel production need to be increasingly concerned with scrap-quality selection.

From the results of numerous investigations it seems that shorter heating times, controlled atmospheres in the reheating furnaces, the application of protective coating or higher temperatures for the hot working are the options in any further investigations. Each option has detrimental and beneficial effects that need to be considered during the steel's hot-processing technology.

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