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2                   **ON THE DAMAGE MECHANISMS IN A CONTINUOUS CASTING MOLD:**

3                   **AFTER-SERVICE MATERIAL CHARACTERIZATION AND FINITE ELEMENT**

4                   **SIMULATION**

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13

14                  **Abstract**

15                  A mold is a part of a continuous casting plant where the molten steel starts to solidify. The inner surface of the

16                  mold undergoes a cyclic thermal load. In fact, service conditions are characterized by a high thermal flux, which

17                  vanishes when the plant is switched off. The highest temperatures occur in the area just beneath the free level of

18                  liquid steel (meniscus). The same area is typically characterized by thermal fatigue cracks when the mold is

19                  inspected after service.

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20 This work presents the characterization of the material of a copper mold after it had been used in the plant. The  
21 aim was to understand the damage and cracking mechanism, and our analysis confirmed that a network of cracks  
22 was present on the inner mold surface in the meniscus area, which experienced the maximum temperature  
23 gradients. Metallurgical examination demonstrated the transgranular characteristics of cracks, thus suggesting that  
24 thermal fatigue was the main cause of the damage observed. The location of the thermal fatigue cracks  
25 corresponded to the area experiencing the highest levels of plastic strains, as confirmed by the results of a finite  
26 element analysis simulating the mold in-service conditions.

27

## 28 **Keywords**

29 Metallurgical examination, Failure analysis, Degradation, Thermal fatigue, Finite element analysis

## 30 **1. Introduction**

31 In continuous casting, the molten steel flows from a tundish into a mold, where it starts to solidify. The mold  
32 is thus a key component of the overall casting process, as it is subjected to high thermal loads and it also controls  
33 the initial shape and quality of semi-finished products (e.g. billets, blooms, slabs), before they enter the rolling  
34 mill lines [1-3].

35 The mold is essentially a water-cooled hollow tube with a rectangular or round cross section. It is usually made  
36 of copper alloy which facilitates an optimal combination of thermal and mechanical properties [3-10]. The inner  
37 surface of the mold is coated with nickel or chromium-based plating to protect the substrate underneath [11-13].

38 When the casting plant is operating, a huge thermal flux  $q$  is transferred from the molten steel, which is in  
39 contact with the inner mold surface, to the water-cooled outer side of the mold (Fig 1). The values of this flux vary  
40 between two conditions:  $q=0$  when the plant is switched off,  $q=q_{\max}$  when the plant is switched on and has reached  
41 full capacity, (Fig 2). The mold is exposed, on its inner surface, to a high time-varying temperature combined with

42 a high thermal gradient across the mold wall. This cyclic thermal loading promotes thermal fatigue cracks in the  
43 meniscus area, which is the most thermally-stressed and strained region of the mold.

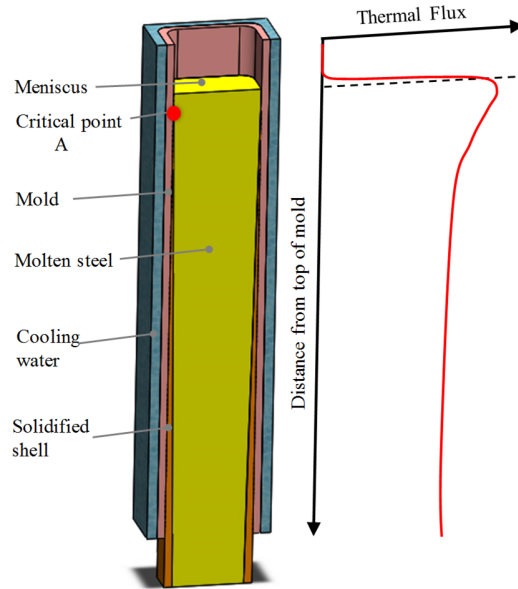


Fig. 1. A mold under working conditions (half section) and axial thermal flux distribution when  $q=q_{max}$ .

44 A mold without cracks ensures safety during the working process and guarantees the quality of the final product  
45 [1, 3]. On the other hand, through-thickness cracks must be avoided as any contact between cooling water and  
46 molten steel would have catastrophic consequences.

47 Several metallurgical studies [2, 8, 11-13] have been performed to determine the complex damage mechanism  
48 that occurs in the mold during its service life. Faries *et al.* [12] observed crack propagation through the copper  
49 substrate with a depth ranging from 0.6 mm to 5 mm. All cracks were found within the area approximately 100÷140  
50 mm from the top of the mold (i.e. 0÷40 mm below the meniscus position). The same observations were reported  
51 by [2, 8, 11] for square and funnel molds.

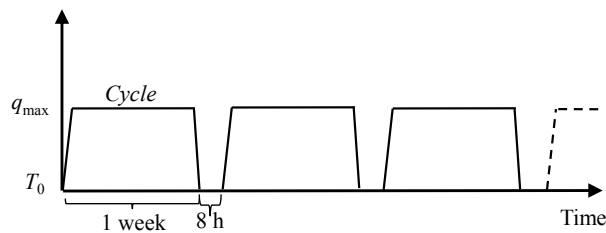


Fig. 2. Variation of the thermal flux during the service life of a mold.

52 The mold in the meniscus zone is damaged because of a detachment of the coating material and mechanical  
53 degradation assisted by the chemical attack of low melting point elements on the Cu substrate which thus becomes  
54 embrittled [1, 2]. The coatings are used to cover the internal walls of the mold, and they are affected by a thermo-  
55 mechanical degradation that reduces the mechanical properties of the deposit [8, 14].

56 The inner surface of the mold undergoes high fluctuating thermal stresses, which can lead to thermal fatigue.  
57 In order to better understand the source of the crack formation and thus to enhance the component service life, we  
58 investigated a possible correlation between the metallurgical observations and the stress and strain distribution in  
59 the cracked area. This work first presents a metallurgical investigation of a copper mold, and then details the results  
60 of a thermo-mechanical analysis performed with numerical techniques.

## 61 **2. Experimental and numerical procedure**

### 62 *2.1 Sample extraction and microstructural characterization*

63 A copper mold with length 1000 mm, rectangular cross section (172 x 174 mm) and thickness 15 mm (see Fig.  
64 3), internally coated with a thin layer of hard Cr, was investigated at the end of its service life. The copper alloy  
65 of the mold had a chemical composition equal to a C14700 alloy, according to ASTM B124B standard [15], see  
66 Table 1.

67

Table 1. Chemical composition of the mold alloy (wt%).

Cu+Ag	P	S
Bal.	0.004	0.3

68

69 First, the copper mold was visually inspected to locate the most damaged areas, from which samples were  
70 subsequently extracted. As illustrated in Fig. 3a, the area near the meniscus is characterized by a wide network of  
71 cracks, while the surrounding parts seem to be unaltered.

72 To characterize the mold microstructure and to determine how cracking takes place, metallurgical  
73 investigations (light microscope and SEM) were performed on a total of five samples extracted from different

74 areas of interest. Two metallographic samples (A1 and A01) were taken from the meniscus area (labeled A in Fig.  
 75 3b), one from the surface center, and one from the corner, respectively. Furthermore, in order to have a complete  
 76 overview of the degradation mechanisms that took place in the mold, three samples were taken from regions  
 77 outside the meniscus zone (labels B1, C1, D1). The samples used for microstructural investigation are presented  
 78 with white squares in Fig. 3b.

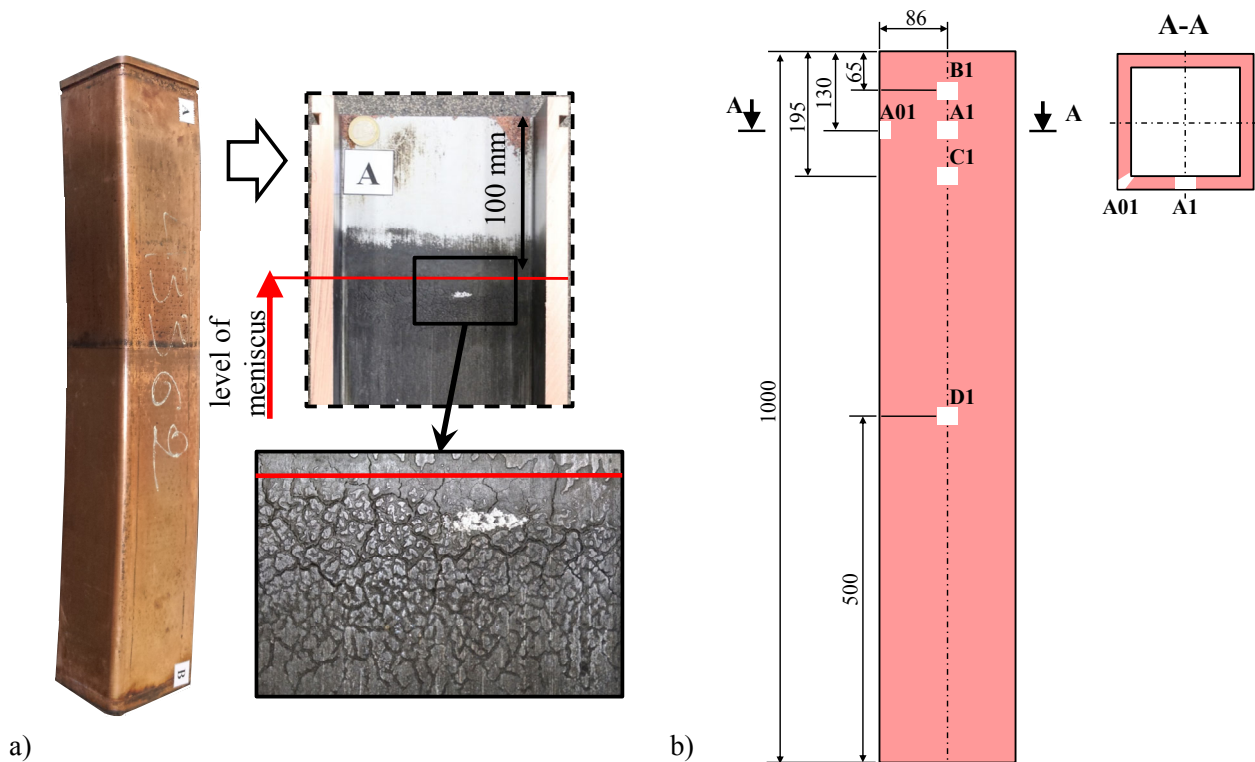


Fig. 3. Mold under investigation with damaged inner surface (a), positions of extracted samples (b).

79 The samples for the metallurgical investigation were extracted from the mold using a refrigerated abrasive  
 80 wheel. Each sample underwent metallographic preparation (embedded in epoxy resin, ground with SiC papers and  
 81 refrigerated with water, and then polished using fabric discs wetted with diamond suspension) in order to obtain a  
 82 mirror-like surface.

83 Before the metallographic preparation, polished samples were analyzed by SEM, in both the cross section and  
 84 the top view (orthogonal and parallel to the original free surface of the mold) to determine the degradation  
 85 mechanisms in each zone of the mold (in the case of samples A01, only the cross section). The same samples were

86 etched, using a solution of  $H_2O:NH_3:H_2O_2=1:1:1$ , and then analyzed by a light microscope to assess the crack  
87 morphology, the grain size (intercept method), and microstructure. Finally, the samples were analyzed by a  
88 stereoscope to identify the crack density (top view) and the average crack depth. The analyses were performed  
89 using the intercept method on the specimens extracted at different positions along the mold height (samples A01,  
90 A1, B1, C1, D1). On the same samples, Vickers micro-hardness profiles were acquired from the external surface  
91 to the core of the mold wall.

92 One specimen was used to measure the chemical composition of the alloy by means of Rf glow discharge  
93 optical emission spectrometry (Rf-GDOES), which was calibrated for bulk analysis of Cu alloys.

## 94 *2.2 Numerical simulations*

95 The thermal stress distribution occurring in the mold was studied with a thermo-mechanical analysis [4-7]. A  
96 three dimensional (3D) finite element model was required, due to the non-uniform distribution of the thermal flux  
97 through the mold length. Since the component has two planes of symmetry and is symmetrically loaded, only a  $\frac{1}{4}$   
98 model with suitable symmetry boundary conditions was considered in the analysis. The mesh was refined close to  
99 the meniscus where the maximum thermal gradient is expected, see Fig. 4.

100 A thermal analysis was performed with an 8-node brick thermal element. The thermal problem is quite complex  
101 as, in principle, it would be necessary to take into account the fluid dynamics of the molten steel (whose  
102 temperature is around 1500 °C), and also the presence of a gap between the steel and mold, which is filled with air  
103 and mold lubricant that acts as an insulating barrier.

104 In this study, the thermal analysis was performed according to the usual simplified procedure [1-3], where a  
105 thermal flux was imposed on the inner surface, while convection was considered on the outer surface of the mold  
106 to simulate water cooling. The red line in Fig. 1 shows the trend of the thermal flux adopted in the analysis, which  
107 was estimated according to the mathematical formulation proposed in [16] and then calibrated with experimental  
108 measurements. The temperature of the cooling water was 40 °C and the convection coefficient was 48000 W/m<sup>2</sup>K.  
109 The convection coefficient was obtained according to the procedure described in [17]. Thermal conductivity was

110 377 W/mK at room temperature and 370 W/mK at 100 °C or above. The time-variation of the thermal flux from  
111 the plant start-up phase to the working condition (and vice versa) was simulated by a sequence of steady state  
112 analyses. In fact, this variation occurs over a relatively short time interval (minutes) compared to the total length  
113 of a whole cycle (days). A nonlinear solution was carried out to simulate the temperature dependence of thermal  
114 properties.

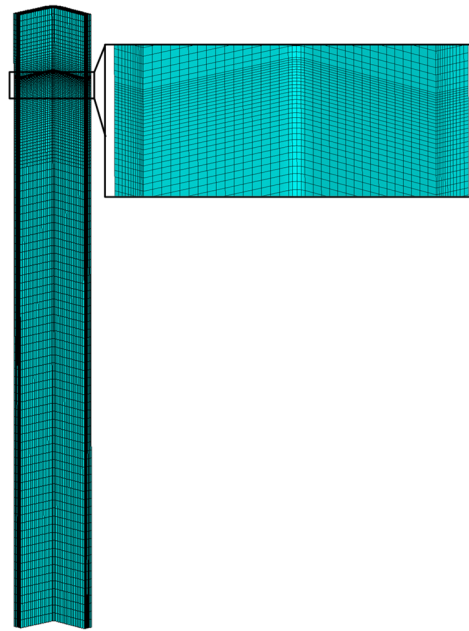


Fig. 4. Finite element model.

115 The temperature distribution calculated previously in the thermal analysis was the input data for the subsequent  
116 mechanical simulation, where structural elements with eight nodes were used. Since the real component is  
117 supported by four slots in the upper part, it can be considered free to expand. Therefore, no mechanical constraints  
118 need to be defined in the finite element model. As a result, the calculated stress-strain distribution only depends  
119 on the temperature distribution in the model. In line with [18], the mechanical load induced by the ferrostatic  
120 pressure was not considered. The dependence of the material parameters on the temperature was also taken into  
121 consideration.

122 With respect to earlier studies [1, 17] that used overly simplified material models (bilinear kinematic), this  
123 study adopted a combined nonlinear kinematic-isotropic material model, whose parameters were estimated from  
124 experimental data under cyclic loading at three temperature levels [9, 19]. The combined kinematic-isotropic

125 model is able to represent simultaneously the Bauschinger effect and the cyclic hardening/softening behavior of a  
 126 material. The von Mises yield criterion can be represented as [20]:

$$127 \quad \sqrt{\frac{3}{2}(\mathbf{S} - \mathbf{X}) : (\mathbf{S} - \mathbf{X})} - R - \sigma_0 = 0 \quad (1)$$

128 where  $\mathbf{S}$  is the deviatoric stress tensor,  $\mathbf{X}$  is the back stress tensor,  $R$  is the drag stress and  $\sigma_0$  is the initial yield  
 129 stress. In this case, the yield surface both translates (controlled by  $\mathbf{X}$ ) and expands (controlled by  $R$ ) with the plastic  
 130 strain  $\varepsilon_p$ . In the literature, several kinematic models have been proposed [20]. The Chaboche model (nonlinear  
 131 kinematic) assumes that the increment in the back stress  $d\mathbf{X}$  is expressed as a function of the plastic strain increment  
 132  $d\varepsilon_{pl}$  and the accumulated plastic strain  $d\varepsilon_{pl,acc}$  [20]:

$$133 \quad \mathbf{X} = \sum_{i=1}^n \mathbf{X}_i \quad ; \quad d\mathbf{X}_i = \frac{2}{3} C_i d\varepsilon_{pl} - \gamma_i \mathbf{X}_i d\varepsilon_{pl,acc} \quad (2)$$

134 where  $C$  is the hardening modulus, and  $\gamma$  is the non-linear recovery parameter. The nonlinear isotropic model  
 135 controls the homothetic expansion of the yield surface [20]:

$$136 \quad dR = b(R_\infty - R)d\varepsilon_{pl,acc} \quad (3)$$

137 where  $R_\infty$  is the saturated drag stress and  $b$  controls the speed of stabilization. Material parameters adopted for  
 138 mechanical simulation are presented in Table 2.

139

Table 2. Material properties for C14700 [9, 19].

Temp. (°C)	$E$ (MPa)	$\sigma_0$ (MPa)	$C_1$ (MPa)	$\gamma_1$	$C_2$ (MPa)	$\gamma_2$	$C_3$ (MPa)	$\gamma_3$	$R_\infty$ (MPa)	$b$
20	119988	113	25880	1627	24460	1624	15620	315.4	-68	2.352
250	106080	110	31310	1708	10240	343.6	5256	1748	-75	3.894
300	103800	108	13170	1092	10700	398.2	10650	1155	-77	5.293

140



141 This combined plasticity model is particularly suitable for thermal fatigue analyses as it enables the stress  
142 evolution over cycles to be accurately calculated. The copper alloy considered in this study showed a typical  
143 softening behavior over cycles, with the yield stress decreasing as the accumulated plastic deformation increased.

### 144 **3. Results**

#### 145 *3.1 Microstructural characterization*

146 Visual inspection revealed that the mold was heavily damaged in the meniscus area, as indicated in Fig. 3a. A  
147 closer examination of the mold inner surface showed that a web of cracks was formed in the area within 100 ÷ 140  
148 mm from the top of the mold, i.e. beneath the level of the maximum thermal flux. In this location, the surface of  
149 the mold generally reaches the highest temperatures. Indeed, in this area the copper mold is in contact with the  
150 molten metal at high temperature, as indicated in Fig. 1. Representative SEM images of the samples A01, A1, B1,  
151 C1 and D1 are shown in Fig. 5 and Fig. 6. As highlighted in Fig. 5, the mold underwent a degradation mechanism  
152 linked to the cracking of the protective coating layer, which was completely detached in samples A01 and A1  
153 (samples extracted in the most thermally-stressed region). In the same region, a thick layer of altered material was  
154 formed in the substrate.

155 The EDXS analyses, see Table 3, showed that the Cu substrate was converted into a brass with a Cu/Zn weight  
156 ratio between 0.5 and 1, which corresponds to the formation of  $\beta'$  (ratio close to 1) and  $\gamma$  (ratio close to 0.5) brittle  
157 phases or a mixture of the two [2, 21, 22]. These phases were full of cracks, mostly in samples A01 and A1. In  
158 sample A1 the crack passed through the brass and continued in the underlying copper substrate. The crack was  
159 surrounded by another phase composed of Zn, S and Pb.

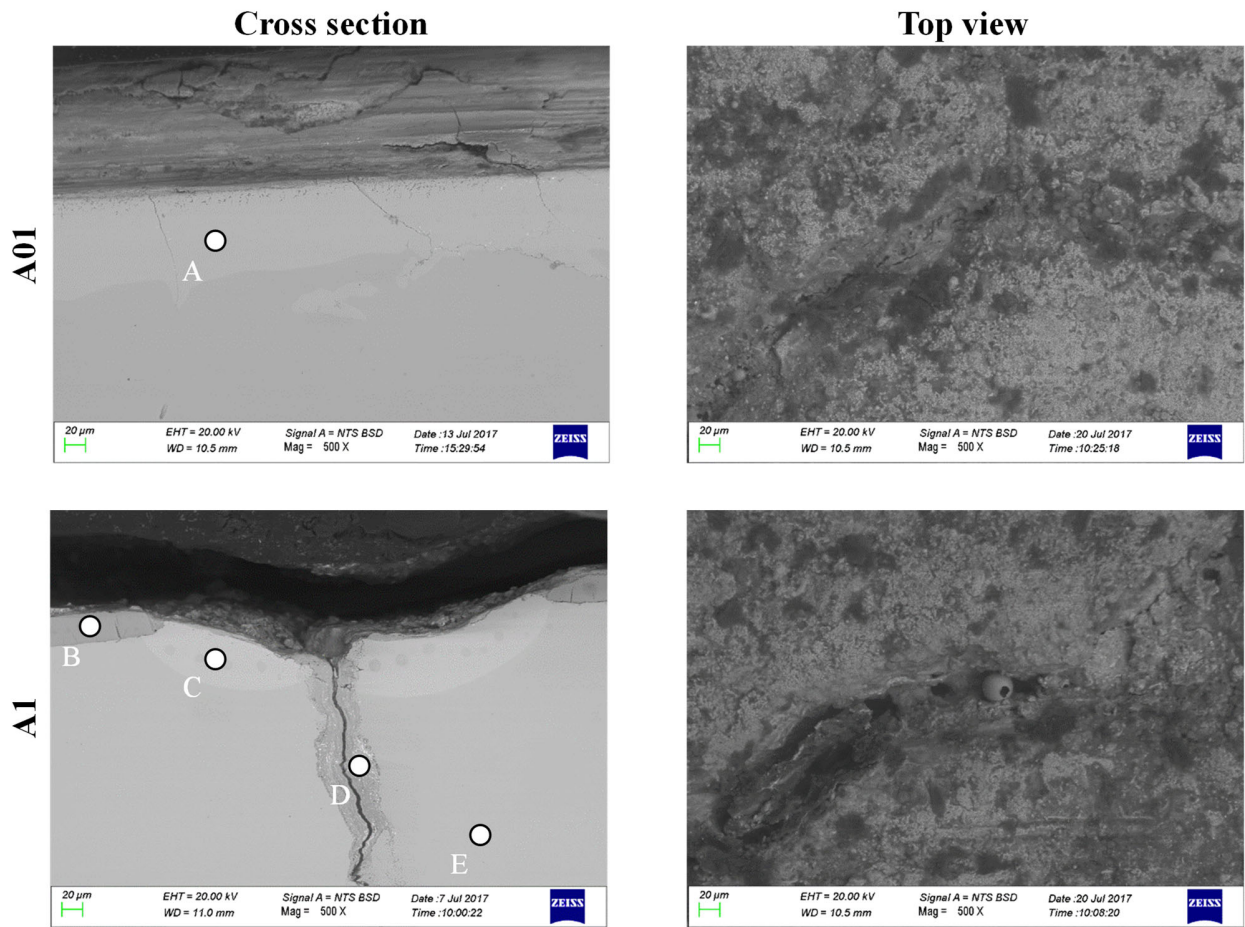


Fig. 5. SEM analysis of samples A01, A1 (top view and cross section). The letters indicate the areas analyzed by EDXS.

160 Samples B1 and C1, which are close to the meniscus area, presented a heavily damaged coating, while the Cu  
 161 material underneath was only slightly affected by chemical degradation, which was the most pronounced in sample  
 162 C1 (arrow), see Fig. 6. The detailed SEM analysis in sample C1 showed the infiltration of low melting point  
 163 elements through the cracks of the coating, see Fig. 7 and Table 4. These elements reached the Cu substrate and  
 164 reacted with it, producing a reaction layer.

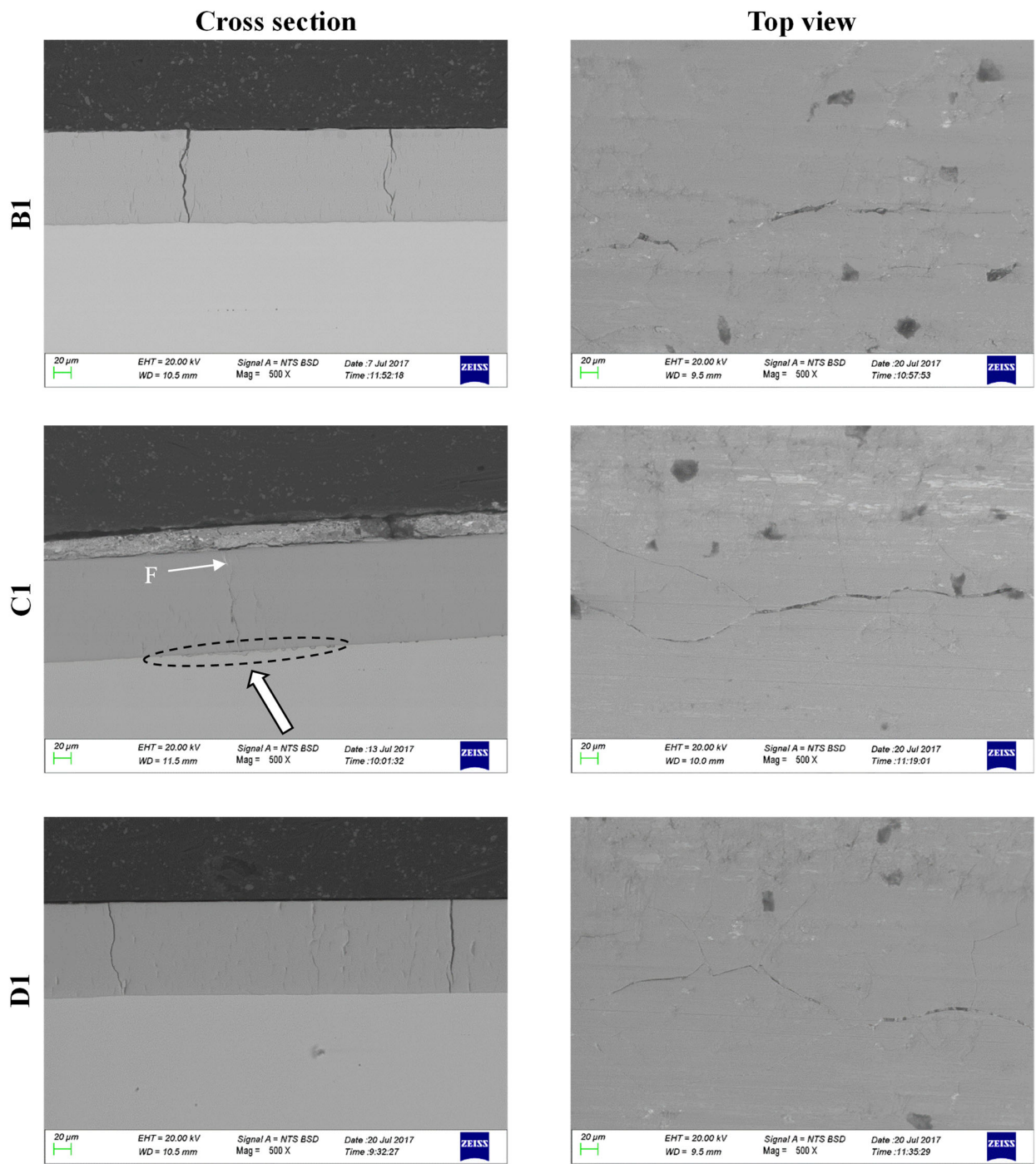


Fig. 6. SEM analysis of the samples B1, C1, D1 (top view and cross section). The letters indicate the areas analyzed by EDXS.

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166  
167  
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Table 3. Semi-quantitative results in weight percentage (wt%) obtained by EDXS analysis in areas highlighted in Fig. 5 and Fig. 6.

Zone under investigation	wt%	S	Mn	Fe	Cu	Zn	Pb	Cr
A					Bal.	66.00		
B					Bal.	62.04		
C					Bal.	65.14		
D		22.04	9.14	1.12	Bal.	20.51	3.20	
E					Bal.			
F		14.83			Bal.		69.24	12.70

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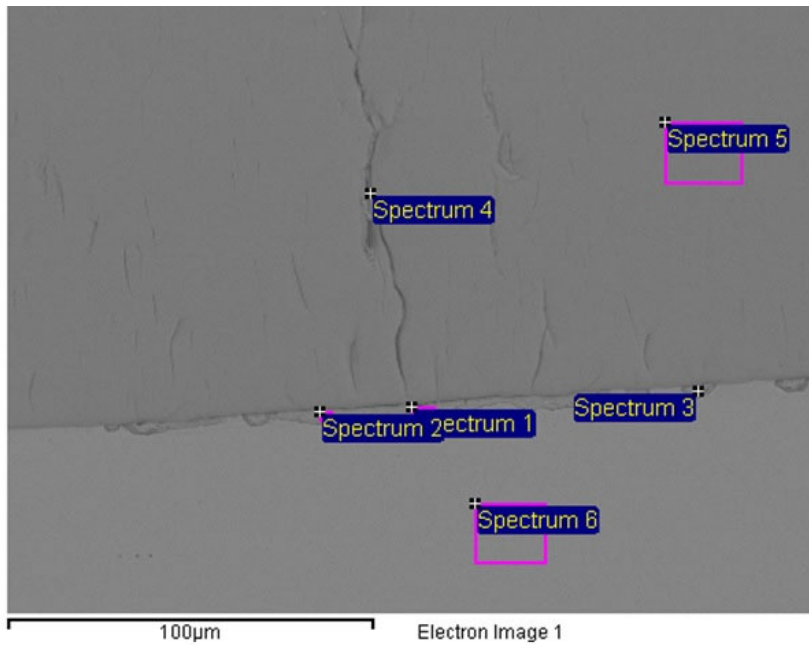


Fig. 7. Detail of the interface of sample C1 (circled area in Fig. 6).

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Table 4. Semi-quantitative results in weight percentage (wt%) obtained by EDXS analysis in areas highlighted in Fig. 7.

Zone under investigation	wt%	S	Cr	Mn	Fe	Cu
Spectrum 1		20.32	3.19			Bal.
Spectrum 2		19.68	4.46			Bal.
Spectrum 3		18.66	3.45	1.74	2.11	Bal.
Spectrum 4			97.50	1.55		Bal.
Spectrum 5			98.19	1.81		Bal.
Spectrum 6						Bal.

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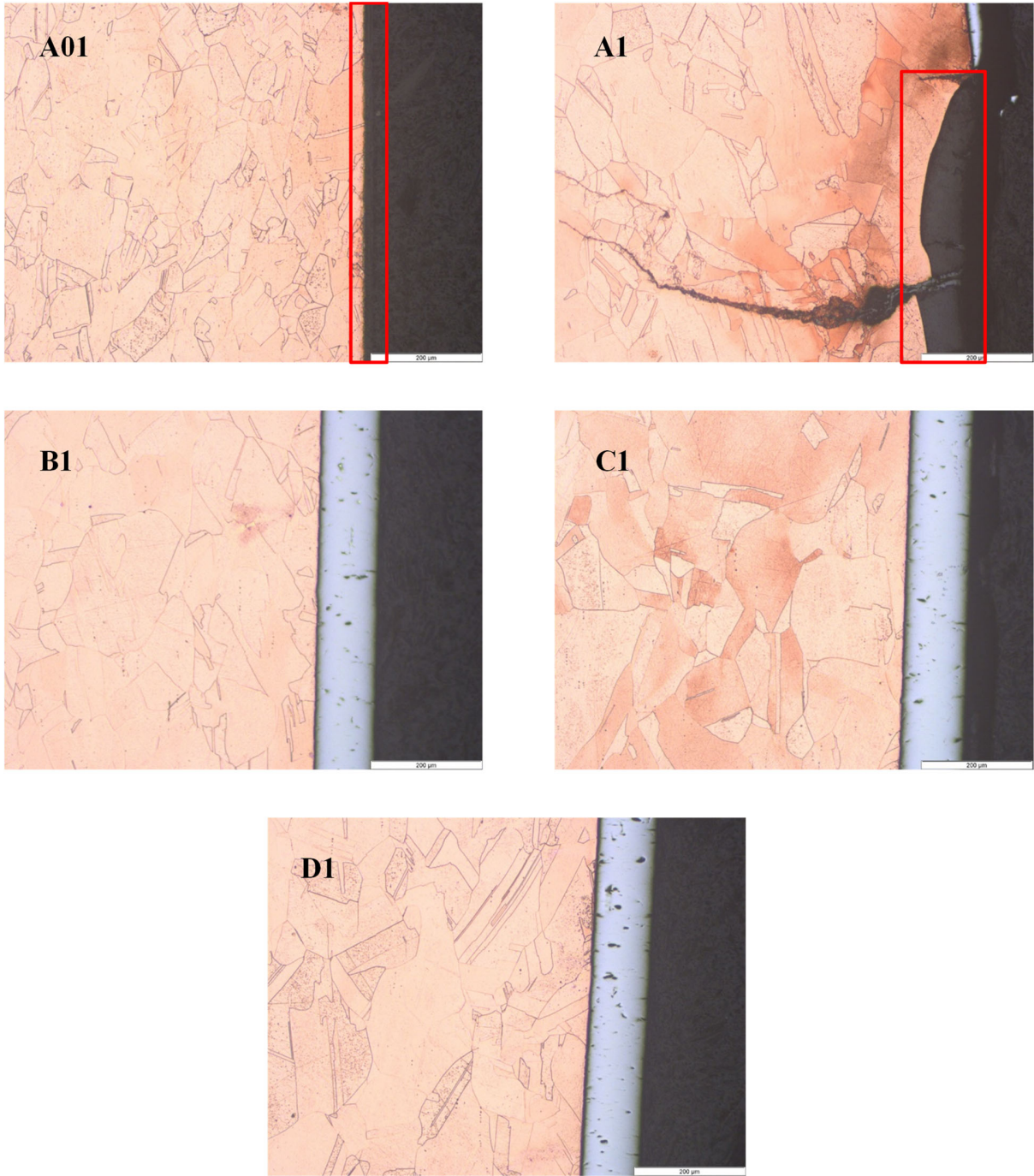


Fig. 8. Microstructural characterization of the analyzed samples.

172 The microstructure of samples A01, A1, B1, C1, D1 is shown in Fig. 8. As already observed by the SEM  
 173 analysis, the light microscopy results confirmed that the mold surface was composed of a Cu substrate coated with  
 174 a layer of hard chromium (0.1 mm thickness). The coating showed many micro cracks and had almost been  
 175 completely removed in the specimens extracted from the meniscus area (A01 and A1). The microstructure of the

176 substrate was composed of austenitic grains in the bulk material (range:  $\sim 70 \pm 30 \mu\text{m}$ ). The grains seem to be coarser  
177 in specimen A1 compared to the other samples. Specimens B1, C1, D1 did not show any microstructural difference  
178 between the core and surface. In addition, samples A01 and A1 presented a surface layer that reacted with the  
179 molten metal (indicated in Figs. 5, 8 and analyzed previously by EDXS), and some cracks that nucleated in the  
180 external reacted layer and propagated to the Cu substrate. The cracks were sharp with transgranular propagation,  
181 and contoured with a slight reaction layer that was previously identified by SEM analysis (Fig. 5 point D). The  
182 morphology of the crack nucleation was barely visible under a light microscope. The SEM analysis of the material  
183 surface (Fig. 9) showed an intergranular crack nucleation in proximity of the surface that had reacted with molten  
184 metal. In this region, the material presented some intergranular morphologies/phases (black arrows) that were  
185 likely to reduce the material toughness locally.

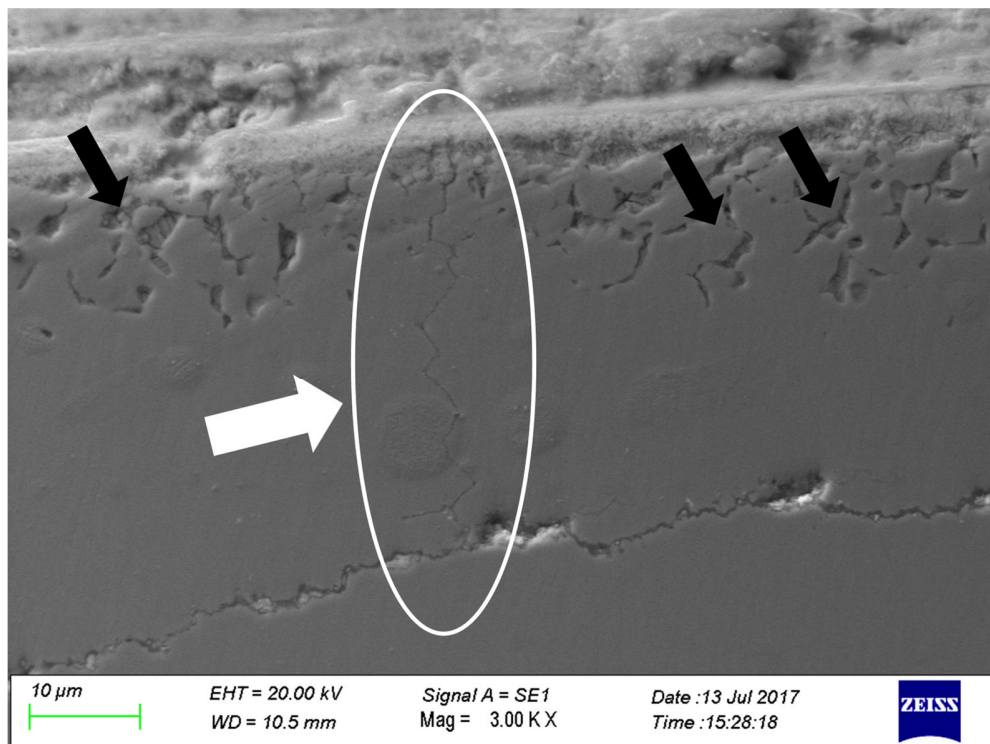


Fig. 9. Detail of the material surface that identifies the crack nucleation morphology. The black arrows indicate the intergranular features. The white circle indicates the intergranular fracture.

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189 The samples extracted in proximity of the meniscus showed several transgranular cracks, as also highlighted  
190 by the microstructural examination. In the meniscus area, the average crack density and average crack depth were  
191 0.3 cracks/mm and 2.8 mm, respectively, in both directions (longitudinal and transversal with respect to the mold  
192 axis). An example of the crack length and morphology, obtained from sample A1, is shown in Fig. 10.

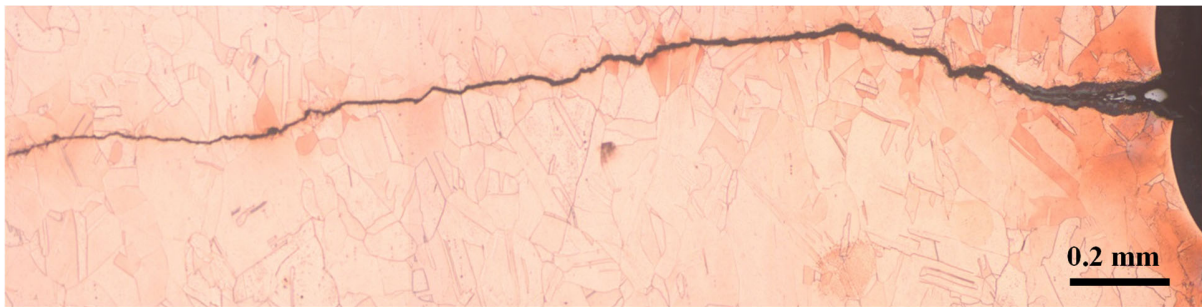


Fig. 10. Image of the crack extension in sample A1.

193 The crack was almost transgranular when it proceeded in the bulk material. The transgranular shape was  
194 maintained in all its length.

195 The micro-hardness profiles are shown in Fig. 11. As highlighted by Fig. 11a, the hardness was higher in  
196 proximity of the surface because of the presence of a hard chromium coating (samples B1, C1, D1) or due to the  
197  $\gamma$  Cu-Zn phase (samples A01, A1). On the other hand, the hardness of the substrate was constant for all the analyzed  
198 samples. Only specimen A1, which was extracted from the center of the mold surface in the meniscus area,  
199 presented a lower hardness value up to a depth of 1-2 mm. These results agreed with the microstructural material  
200 characterization that exhibited a coarser microstructure in sample A1 compared to the others.

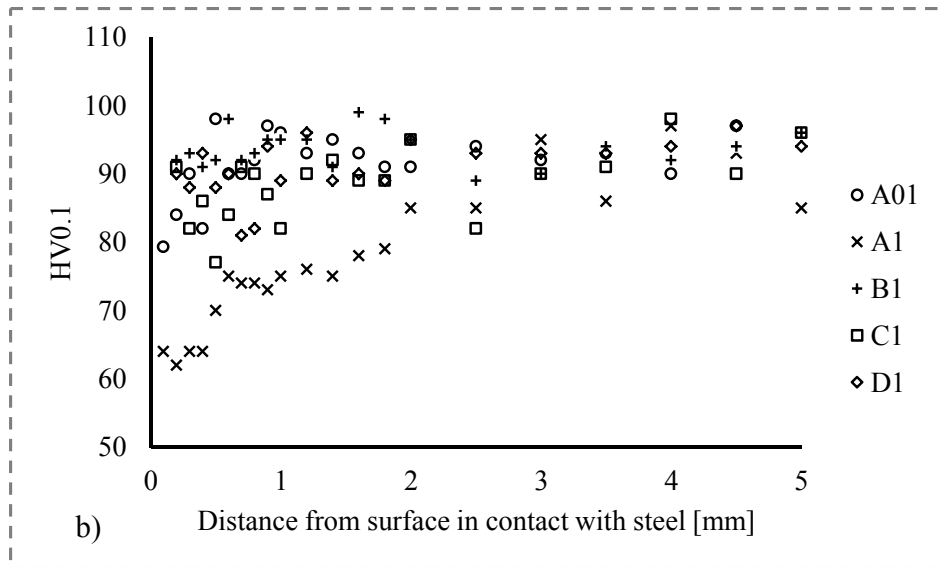
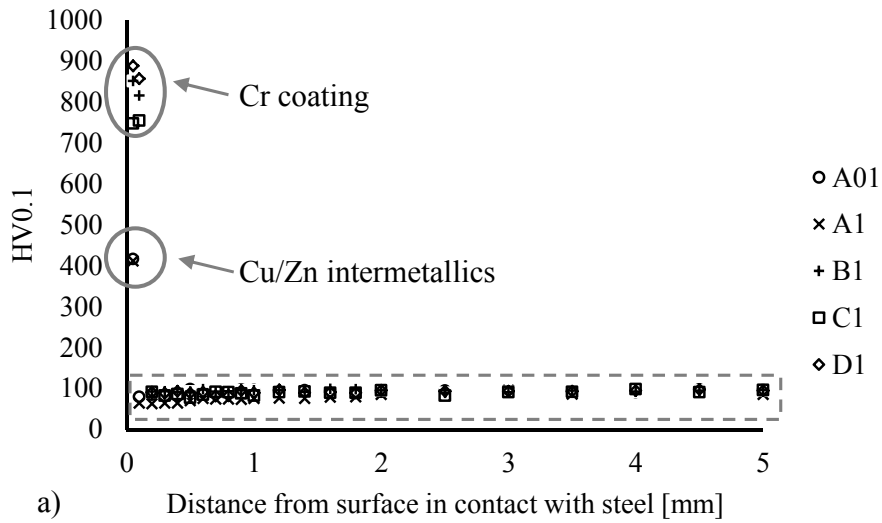


Fig. 11. Micro-hardness profiles for the tested specimens: a) complete profile, b) zoom of the hardness between 50 and 110 HV0.1 (square area of Fig. 11a).

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### 3.2 Thermo-mechanical results

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The temperature distribution obtained at the maximum thermal flux is presented in Fig. 12a. The highest temperature was observed at 30 mm below the position where the maximum flux was applied, at the point labeled with the letter “A”, where the largest through-thickness thermal gradient also occurred.



206 The von Mises stress distribution is shown in Fig. 12b. The stresses also exceeded the yield stress in those  
 207 regions of the inner mold surface in which the thermal flux attained its largest values. This is also evidenced in  
 208 Fig. 12c, which displays the von Mises plastic strain distribution. The maximum plastic strains were located where  
 209 the highest temperature occurred.

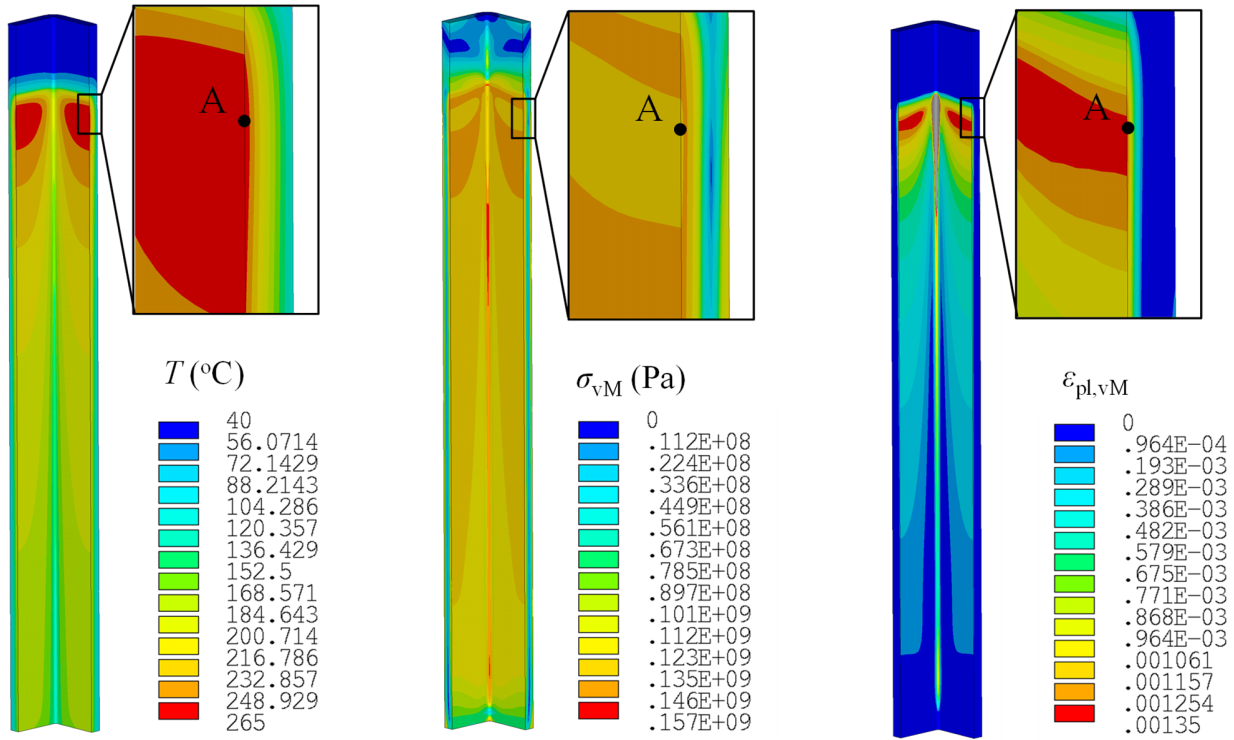


Fig. 12. Numerical model: a) temperature distribution at  $q_{\max}$ , b) von Mises stress distribution, c) von Mises plastic strain distribution.

210 Fig. 13 and Fig. 14 present the through-thickness variation of the three stress components (hoop, axial and  
 211 radial) calculated at point A, when the mold undergoes the thermal flux (*hot-phase*) and during the plant switch  
 212 off due to maintenance (*cold-phase*), respectively. Hoop and radial components were parallel and perpendicular  
 213 to the mold surface, respectively, whereas the axial component was along the mold axis. A biaxial state of stress  
 214 occurred in the analyzed component. In the *hot* and *cold-phase*, both the hoop and axial stress followed a similar  
 215 trend through the wall thickness, while the radial component was negligible. Indeed, once the plant has been  
 216 switched on, the molten steel heats the inner part of the mold, whose temperature rapidly increases until the  
 217 operating condition is fully reached (*hot-phase*). The outer part of the component is maintained at a lower  
 218 temperature due to the presence of the cooling fluid. It follows that the inner hot portion of the mold tends to

219 expand, but is constrained by the outer colder part. As a consequence, rather high compressive stresses occurred  
 220 inside the mold and in the hottest area they even exceeded the material yield stress, see Fig. 13.

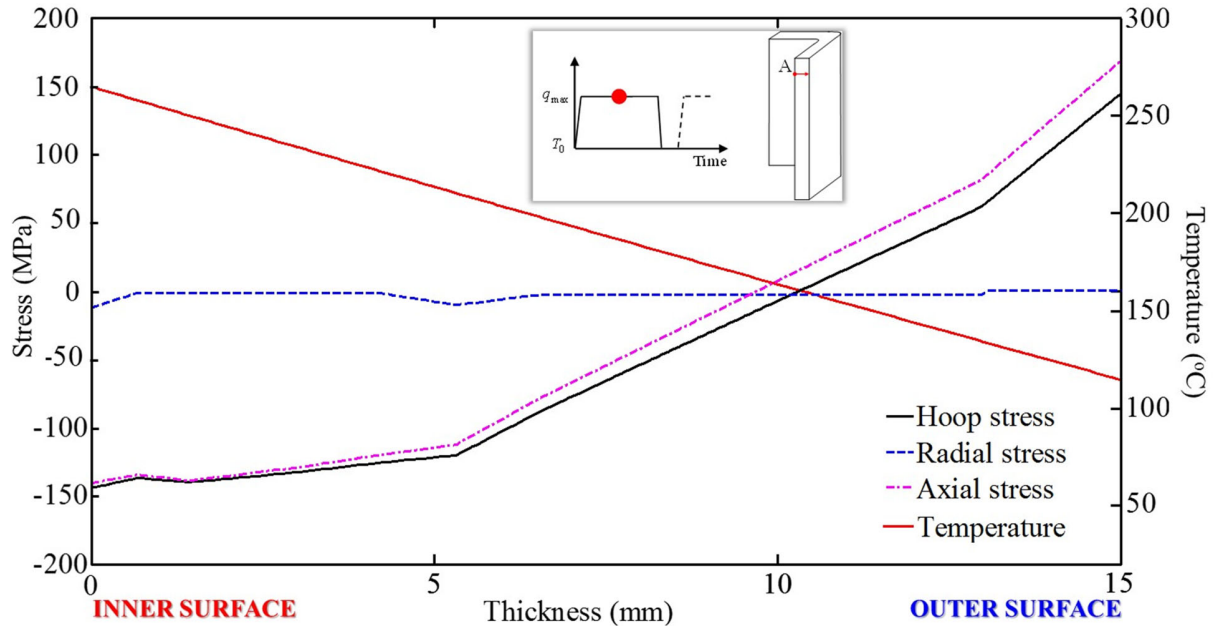


Fig. 13. Stress and temperature distribution versus thickness at the critical point A – *Hot-phase*.

221 The opposite occurs when the plant is switched off (*cold-phase*). In the latter case, the mold is cooled down to  
 222 room temperature and consequently the zone plasticized during heating undergoes tensile stresses (Fig. 14).

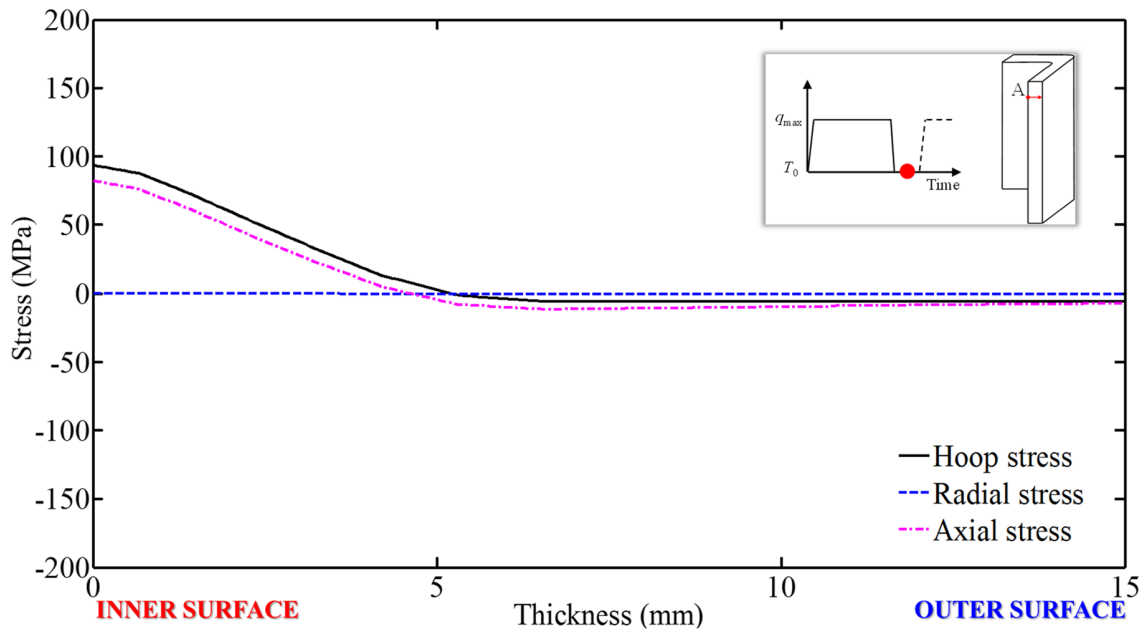


Fig. 14. Stress distribution versus thickness at the critical point A – *Cold-phase*.

223 **4. Discussion**

224 The experimental results showed that the damage mechanism of the copper mold was related to the synergistic  
225 effect of thermal fatigue and chemical/metallurgical degradation. This was confirmed by the visual inspection  
226 (Fig. 3a) which revealed severe damage close to the meniscus area, accompanied by the complete detachment of  
227 Cr coating. Indeed, the numerical analysis revealed the presence of high thermal stresses in the proximity of the  
228 meniscus area (Fig. 12) due the high thermal gradient reached in the *hot-phase*.

229 Owing to the plant being switched on/off continually, the stresses in the inner mold surface fluctuate from  
230 negative (compressive) values, approaching yielding, up to positive (tensile) values. These fluctuating stresses  
231 cause a thermal fatigue phenomenon, as demonstrated by several cracks mainly observed close to the meniscus  
232 area (i.e. in the position of sample A1 followed by A01), where temperatures are higher. According to O'Connor  
233 and Dantzig [8], the tensile stresses are responsible for damages that occur on the inner surface near the meniscus.  
234 Fig. 15 compares the inner surface of the real component and the distribution of the von Mises plastic strain,  
235 evaluated numerically in the same area. The most critical area (where the highest plastic strain values occur) is  
236 located where the cracks were observed with the metallurgical analysis.



Fig. 15. Comparison between the mold inner surface and the von Mises plastic strain distribution.

237 The experimental analyses of the damaged areas in the mold highlight that samples A1 and A01 were the most  
238 damaged. The SEM cross section analyses of the samples showed the presence of a Cu-Zn layer from which the  
239 cracks nucleated and then propagated in the Cu substrate. The Cr coating was completely detached in the meniscus  
240 area. The Cr detachment was the first damage that occurred in the Cu mold, which seems to be linked to the thermal  
241 fatigue to which the mold was subjected during the service life.

242 The difference in the thermal expansion coefficient between the Cu and the hard Cr coating [23] is the main  
243 cause of the coating failure. In this case, it is supposed that the highest stresses are located in the proximity of the  
244 interface between the substrate and the coating. Crack propagation as well as coating detachment are very rapid  
245 because, according to [24], micro-cracks already appear in an *as deposited* condition due to the brittle nature of  
246 the coating. As indicated by Hadavi *et al.* [14], the Cr coating undergoes a reduction of hardness during the high  
247 temperature exposure that lowers the mechanical properties (hardness, fatigue). The failure of the coating leads to  
248 an infiltration of low melting point elements (Zn, S, Pb), which are probably expelled during the solidification of  
249 the steel because of their low solubility or because they form low melting point compounds. These elements, which  
250 present a high affinity with Cu, infiltrate the cracks of Cr coating and generate a liquid metal infiltration, which  
251 presents a morphology similar to an undermining corrosion of the coating [2, 14, 21, 22, 25]. The coating is then  
252 detached and the bare Cu is exposed to the deleterious low melting point elements. In this case, the reaction of  
253 these elements with Cu is fast and controlled by the diffusion. In the meniscus zone, the Cu substrate reacts first  
254 with Zn, which forms brittle intermetallic phases ( $\gamma$  brass,  $\beta'$  brass or mixture of two). Furthermore, this brittle  
255 phase breaks, nucleating the thermal fatigue crack of the substrate, which propagates in the Cu alloy [2, 11]. The  
256 crack nucleation is intergranular (Fig. 9) and favored by the precipitation of intermetallic phases at grain  
257 boundaries. The crack propagation, instead, is transgranular (Fig. 10) and is enhanced by the infiltration of  
258 elements with a lower melting point temperature than Zn, as Pb and S (Fig. 5). In this case, probably because of  
259 the lower temperature inside the crack compared to the temperature of the internal wall of the mold, these elements  
260 infiltrate more in the crack than in the top surface. The result is a reaction of these elements with the Cu that  
261 produces brittle phases in the crack tip, which enhance the crack propagation of the thermal fatigue crack. The  
262 crack propagation in sample A1 was also favored by a possible grain growth of the Cu substrate that reduced

263 locally the toughness of the material. The grain growth could be a consequence of the long time exposure of the  
264 material after the recrystallization process, as suggested by Barella *et al.* [11]. This was confirmed by both micro-  
265 hardness results and the metallographical investigation of the material. On the other hand, the specimen extracted  
266 from the corner presented the same degradation mechanism as the sample extracted from the meniscus area  
267 although it seemed to be exposed to less invasive thermo-mechanical damage (Fig. 5, Fig. 6 and Fig. 8).

268 The numerical thermal analysis identified the corners as the regions at the meniscus level that experienced a  
269 lower temperature (Fig. 12). Instead, specimens B1 and C1 (extracted in the areas away from the meniscus zone  
270 and exposed to the lower temperatures) showed a lower kinetics of infiltration (Fig. 7 and Tab. 4). This  
271 phenomenon is still present and linked to elements with a lower melting temperature than Zn (mainly S). The  
272 specimens D1 extracted from the coldest zone of the mold revealed the thermal fatigue cracking mechanism of the  
273 Cr coating quite clearly. In this case, because of the lower temperatures and the slowest infiltration of low melting  
274 point elements, the degradation mechanism was not completely developed as in the samples extracted from the  
275 meniscus.

## 276 **5. Conclusions**

277 The present work investigated the degradation mechanisms of a continuous casting mold after service. The  
278 experimental results showed that the meniscus area, which is the most stressed region of the mold, was heavily  
279 damaged by a thermo-mechanical degradation assisted by a chemical attack of the underlying material. In the early  
280 damage phase, degradation involves the complete detachment of the Cr coating used to protect the substrate  
281 underneath. Subsequent degradation is due to the liquid metal infiltration of low-melting point elements that  
282 embrittle the substrate directly exposed to the molten steel. These elements make thermal fatigue cracks nucleate  
283 and then propagate in the most critical area evidenced by FEM simulation in term of the most stressed locations.

284 Alternative coatings to the hard chromium plating (e.g. thermal spray coatings, binary/ternary alloys deposited  
285 by electrodeposition) could be adopted in order to delay the coating detachment and thus increase the mold service  
286 life. It would also be beneficial to decrease the amount of low melting point elements in the steel.

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290 **References**

- 291 1 Park, J.K., Thomas, B.G., Samarasekera, I.V., Yoon, U.S. (2002) Thermal and mechanical behavior of  
292 copper molds during thin-slab casting (I): plant trial and mathematical modeling, *Metallurgical and*  
293 *Materials Transactions B*, **33B**, 1-12.
- 294 2 Park, J.K., Thomas, B.G., Samarasekera, I.V., Yoon, U.S. (2002) Thermal and mechanical behaviour of  
295 copper molds during thin slab casting(II): Mold crack formation, *Metallurgical and Materials Transactions*  
296 *B*, **33B**, 437-449.
- 297 3 Thomas, B.G. (2001) Continuous Casting of Steel. Chapter 15 in Modeling for casting and solidification  
298 processing, Dekker, M. (Ed.), New York, 499-540.
- 299 4 Srnec Novak, J., Stanojevic, A., Benasciutti, D., De Bona F. and Huter, P. (2015) Thermo-mechanical finite  
300 element simulation and fatigue life assessment of a copper mould for continuous casting of steel, *Procedia*  
301 *Engineering*, **133**, 688–697.
- 302 5 Moro, L., Srnec Novak, J., Benasciutti, D., De Bona, F. (2017) Copper mold for continuous casting of steel:  
303 Modelling strategies to assess thermal distortion and durability, *Key Engineering Materials*, **754**, 287-290,  
304 DOI:10.4028/www.scientific.net/KEM.754.287.
- 305 6 Moro, L., Srnec Novak, J., Benasciutti, D., De Bona, F. (2017) Thermal distortion in copper moulds for  
306 continuous casting of steel: Numerical study on creep and plasticity effect, *Ironmaking and Steelmaking*, in  
307 press (DOI: 10.1080/03019233.2017.1371425).
- 308 7 Moro, L., Benasciutti, D., De Bona, F. (2017) Simplified numerical approach for the thermo-mechanical  
309 analysis of steelmaking components under cyclic loading: an anode for electric arc furnace, *Ironmaking and*  
310 *Steelmaking*, in press (DOI:10.1080/03019233.2017.1339482).
- 311 8 O’Connor, T.G., Dantzig, J.A. (1994) Modeling the thin-slab continuous-casting mold, *Metallurgical and*  
312 *Materials Transactions B*, **25B**, 443-457.
- 313 9 Benasciutti D., Srnec Novak J., Moro L., De Bona F., Stanojevic A. (2018) Experimental characterization  
314 of a CuAg alloy for thermo-mechanical applications. Part 1: Identifying parameters of non-linear plasticity  
315 models, *Fatigue & Fracture of Engineering Materials & Structures*, **41**, 1364-1377,  
316 DOI:10.1111/ff3.12783.
- 317 10 Benasciutti D., Srnec Novak J., Moro L., De Bona F. (2018) Experimental characterization of a CuAg alloy  
318 for thermo-mechanical applications. Part 2: design strain-life curves estimated via statistical analysis,  
319 *Fatigue & Fracture of Engineering Materials & Structures*, **41**, 1378-1388, DOI:10.1111/ff3.12781.
- 320 11 Barella, S., Gruttaduria, A., Mapelli, C., Mombelli, D. (2014) Investigation of failure and damage on a  
321 continuous casting copper mould, *Engineering Failure analysis*, **36**, 432-438.
- 322 12 Faries, F., Rawson, J., Rose, A., Bugdol, M. (1996) Mould coatings for continuously cast billet production,  
323 Technical steel research – Final Report.
- 324 13 Pandey, J. C., Raj M., Mishra, R., Tripathy, V.K., Bandyopadhuau N. (2008) Failure of nickel coating on a  
325 copper mold of a slab caster, *Journal of Failure Analysis and Prevention*, **8**, 3-11.

- 326 14 Hadavi, S.M.M., Zadaeh, A. A., Jamshidi, M.S. (2004) The effect of thermal fatigue on hardness of hard  
327 chromium electroplating, *Journal of Materials Processing Technology*, **147**, 385-388.
- 328 15 ASTM B 124 - B 124M (2008) Standard specification for copper and copper alloy forging rod, bar, and  
329 shapes.
- 330 16 Udayraj, Chakraborty, S., Ganguly, S., Chacko, E.Z., Ajmani, S.K. and Talukdar, P. (2017) Estimation of  
331 surface heat flux in continuous casting mould with limited measurement of temperature, *International*  
332 *Journal of Thermal Sciences*, **118**, 435-447.
- 333 17 Samarasekera, I.V. (1980) Thermal distortion of continuous casting mould, Thesis, The University of  
334 British Columbia, Vancouver, Canada.
- 335 18 Thomas, B.G., Li, G., Moitra, A. and Habing, D. (1997) Analysis of thermal and mechanical behavior of  
336 copper molds during continuous casting of steel slabs, 80<sup>th</sup> Steelmaking Conference, Chicago, USA.
- 337 19 Srnec Novak, J., Benasciutti, D., De Bona, F., Stanojevic, A., De Luca, A. and Raffaglio, Y. (2016)  
338 Estimation of material parameters in nonlinear hardening plasticity models and strain life curves for CuAg  
339 alloy, IOP Conf. Series: *Materials Science and Engineering*, 119, 012020.
- 340 20 Lemaitre, J., Chaboche, J.L. (1990) Mechanics of solid material, Cambridge University Press, Cambridge.
- 341 2116 Davis, J.R. (2001) Copper and copper alloys, First edition, ASM International, Ohio.
- 342 22 Gravemann, H. J., Brown, I., Tapley, C.D. (1981) Continuous casting of steel, 2nd process technology  
343 conference, Chicago, IL, **2**, 23-25.
- 344 23 Various authors (1990) ASM Metal handbook vol2: Properties and selection: Non-ferrous alloys and  
345 special-purpose materials, First edition, ASM International, Ohio.
- 346 24 Cotell, C.M., Sprague, J.A., Smidt Jr, F.A. (1994) ASM Metal Handbook Vol. 5: Surface engineering, First  
347 edition, ASM International, Ohio.
- 348 25 Korb, L.J. and Olson, D.L. (1992) ASM Metal handbook Vol. 13: Corrosion, Fourth edition, ASM  
349 International, Ohio.

350 FIGURE CAPTIONS

351

352 Fig. 1. A mold under working conditions (half section) and axial thermal flux distribution when  $q=q_{\max}$ .

353 Fig. 2. Variation of the thermal flux during the service life of a mold.

354 Fig. 3. Mold under investigation with damaged inner surface (a), positions of extracted samples (b).

355 Fig. 4. Finite element model.

356 Fig. 5. SEM analysis of samples A01, A1 in top view and cross section. The letters indicate the areas analyzed by EDXS.

357 Fig. 6. SEM analysis of samples B1, C1, D1 in top view and cross section. The letters indicate the areas analyzed by  
358 EDXS.

359 Fig. 7. Detail of the interface of sample C1 (circled area in Fig. 6).

360 Fig. 8. Microstructural characterization of the analyzed samples.

361 Fig. 9. Detail of the material surface that identifies the crack nucleation morphology. The black arrows indicate the  
362 intergranular features. The white circle indicates the intergranular fracture.

363 Fig. 10. Image of the crack extension in sample A1.

364 Fig. 11. Microhardness profiles for the tested specimens: a) complete profile, b) zoom of the hardness between 50-110  
365 HV0.1 (square area of Fig. 11a).

366 Fig. 12. Numerical model: a) Temperature distribution at  $q_{\max}$ , b) von Mises stress distribution, c) von Mises plastic strain  
367 distribution.

368 Fig. 13. Stress and temperature distribution versus thickness at of the critical point A – *Hot-phase*.

369 Fig. 14. Stress distribution versus thickness at of the critical point A – *Cold-phase*.

370 Fig. 15. Comparison between the mold inner surface and the von Mises plastic strain distribution.