EFFECTS OF COPPER ADDITION ON DELAYED CRACKING PHENOMENON OF DEEP-DRAWN AND REDRAWN CUPS OF AUSTENITIC STAINLESS STEELS

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Abstract. *Metastable austenitic stainless steels show the Delayed Cracking Phenomenon when they are significantly deformed by deep drawing operation. This phenomenon occurs in those steels that transform substantially to martensite during forming. Copper is an alloying element that can partially inhibit this transformation making austenite more stable against strain induced martensitic transformation. The purpose of this investigation was to evaluate both the effect of copper addition on the amount of α' martensite formed along the cup wall of austenitic stainless steel deep-drawn and redrawn cups and the number of cracks appearing in the cups edges due to the Delayed Cracking Phenomenon. Also in this work, the same features of a conventional metastable austenitic stainless steel are presented in order to compare to copper-added steel.*

Keywords *Delayed Cracking Phenomenon, strain induced martensite, austenitic stainless steel*

1. Introduction

Metastable austenitic stainless steels, such as AISI type 304, are used in the production of a wide variety of formed and drawn parts for architectural, automotive, industrial, domestic applications and in the food and pharmaceutical industries. Equipments made of these materials are indicated for many applications in the chemical industry, since they show high corrosion resistance and very smooth surfaces, avoiding accumulation of impurities and optmizing cleaning procedures (Acesita, 2002). Most of these applications demand good performance during fabrication steps, since they will be press-formed into a more complicated shape or the material will be deep-drawn to a required depth without intermediate annealing (Ikegami *et al*., 1999).

Austenitic stainless steels attain good ductility and improved stretch formability resulting from strain-induced martensitic transformation (Rintamaa *et al*., 1982; Gonzalez *et al*., 2003) which are adequate to press-forming performance. However, their deep drawability is not so good as the others properties. In addition, metastable austenitic stainless steels are susceptible to Delayed Cracking Phenomenon when the sheets of these materials are heavily deep-drawn (Ikegami *et al*., 1999).

The Delayed Cracking Phenomenon, that is observed in successfully deep-drawn cups, is characterized by the appearance of cracks in the top edge of the cups in a matter of hours, or even days or months after the forming (Schaller *et al*., 1972; Frehn and Bleck, 2003). The phenomenon, which occurs only in those steels that transform substantially to martensite during forming (Schaller *et al*., 1972), is related to the residual stresses that remain in the parts due to the different strain levels experienced in different locations of the workpiece caused by difference in strength between different but co-existent phases in the material, or different strains in different locations and or else, a possible gradient temperature. (Wang and Gong, 2002). These stresses are largest near the top of the walls and they can lead to splitting of them by cracking unless the cups are stress relieved (Hosford and Caddell, 1983).

In austenitic stainless steels, the sensivity to the phenomenon is determined by the volume fraction of martensite (Hoshino, 1977) which in turn is a function of the chemical composition of the steels (Gonzalez *et al*., 2003). Frehn and Bleck (2003) have reported the existence of an α' martensite gradient through the cup walls. According to these authors, the phenomenon was observed in austenitic stainless steels which have formed high amounts, over 35%, of α' martensite during deep drawing process, or respectively, showed a high gradient of that phase. This gradient was responsible for residual stresses in the cup wall which could lead to the Delayed Cracking Phenomenon.

The formation of α' martensite phase is related to the austenite stability: the more stable the austenite phase, the less martensite is formed. The stability of austenite in relation to the α' martensite transformation is determined by the chemical composition and usually evaluated by the Md_{30} parameter, that is the temperature at which 50% of α' martensite is obtained in a tension test for a true deformation of 0.3 (Angel, 1954).

Alloying elements like nickel, copper, carbon and nitrogen have strong effects on the austenite stability and Delayed Cracking Phenomenon. According to Kim *et al*. (1999), Delayed Cracking occurs largely with low nickel steels. On the other hand, lowering carbon and nitrogen contents and enhancing the copper amount may improve the susceptibility of the Delayed Cracking of this class of steels.

Nohara *et al*. (1977) have shown that copper has the same influence of nickel on the Md_{30} temperature, which decreases with increasing amounts of these elements. Furthermore, copper is an effective element for the improvement of deep drawability of austenitic stainless steels (Ikegami *et al*., 1999) and because it raises their stacking fault energy. This parameter is known to influence the mechanical behavior of this class of stainless steels.

The purpose of this research was to evaluate the effects of copper addition to a commercial AISI type steel on the amount of α' martensite formed along deep drawn and redrawn cup walls and relate it to Delayed Cracking Phenomenon. The Delayed Cracking behavior of a conventional AISI 304 was also presented in order to compare it to the copper added Delayed Fracture behavior.

2. Experimental Procedures

The chemical compositions and the calculated Md_{30} temperature according to Equation 1 (Nohara *et al*., 1977) of the copper-added (labeled N) and one conventional (labeled B) steels used in this study are shown in Tab. 1. Both the steels are commercial grades of AISI 304.

$$\begin{aligned} Md_{30} &= 551 - 462(\%C + \%N) - 9.2(\%Si) - 8.1(\%Mn) - 13.7(\%Cr) \\ &- 29(\%Ni + \%Cu) - 18.5(\%Mo) - 68.9(Nb) - 14.2(TG - 8) \end{aligned} \tag{1}$$

Table 1: Chemical compositions of B and N austenitic stainless steels (in weight percent) and Md_{30} temperatures (in degree Celsius).

Steel	C	N	Si	Mn	Cr	Ni	Cu	Mo	Nb	Md30
B	0.0255	0.047	0.31	0.443	18.23	8.91	0.225	0.126	0.012	-13.7
N	0.033	0.035	0.44	0.99	18.07	8.06	1.601	0.099	-	-34.3

This table indicates that nickel content of N stainless steel was slightly reduced, meanwhile its copper amount was enhanced. The steels were supplied as 0.6 mm thick cold rolled and annealed sheets.

Both the two steels used to evaluate the susceptibility to the Delayed Cracking Phenomenon were subjected to the double step drawing method by using an Erichsen 142-40 forming machine. N and B steels sheets were drawn at different drawing rations (DR) by changing the various blank diameters (56, 60, 64), using a 33mm punch diameter. The redrawn operation was performed with a 26mm punch diameter. Both the forming operations were conducted at room temperature with a 600mm/min deep drawing rate. In order to avoid wrinkle formation in the flange area, a blank holder was used which was pressed with pressures of 10-12kN against lubricated (with molybdenum bisulfate ad PVC sheet) plates. In the redrawing operation, the pressures have ranged of 4 to 6kN.

After the cups were redrawn, they were held at room temperature, at least for 24h, to observe whether cracking did occur or not. If, at least one of several redrawn cups cracked at a certain drawing ratio, this drawing ratio was determined as the limited drawing ratio of the delayed cracking (LDR-DC). The cups were kept in room temperature and periodically (every 24h) observed to count the number of cracks opened in the cups edges. It was observed 15 drawn and redrawn cups and the average number of cracks in the redrawn cups were determined dividing the total number of cracks appeared by the number of cups.

After the forming tests, volume fractions of strain induced martensite formed along the drawn and redrawn cup walls were measured by X-ray diffraction. The semi-quantitative determination of volume fraction of phases by X-ray diffraction was based on the principle that the total integrated intensity of all diffraction peaks of each phase in a mixture is proportional to the volume fraction of that phase.

Small round specimens were cut from the cup walls for X-ray diffraction in a Metals Research Servomet Spark machine. The Servomet removes metal from the area in the immediate vicinity of the tool without mechanical contact with the work by generating a series of controlled spark discharges. Each spark removes a small crater of metal by melting and vaporization.

In order to remove the effects of cutting and surface impurities on the transformation response, diffraction patterns were obtained on samples chemically etched to remove a fraction of the samples thickness. The solution used for surface removal was a mixture of hydrochloric acid, nitric acid, acetic acid, glycerin and distilled water.

X-ray diffraction analysis was performed in a Philips PW70 Diffractometer using Cu Kα radiation and a graphite crystal monochromator. A sample holder was specially designed to fix the specimens in the equipment. This sample holder can be seen in the Fig. 1:

Figure 1: Sample holder with specimen used for the measurement of the amount of α'martensite.

After the determination of the volume fraction of martensite, the same round samples were chemically polished with a perchloric acid, ethanol and distilled water solution and etched with Aqua Regia or oxalic acid. The following parameters were used to polish the samples: current density: 0.2-0.4A and exposition time: 10s. The polished samples were rinsed in ethanol. The microstructure features of the strain induced martensite were observed by optical microscopy.

3. Results and Discussion

3. 1 The Susceptibility of the Formed Cups to The Delayed Cracking Phenomenon

Figure 2 shows a redrawn cup of B austenitic stainless steel for a drawing ratio of 1.9. It has observed that Delayed Cracking Phenomenon appears only in the redrawn cups formed with B stainless steel (as indicated by arrow). So, this drawing ratio was the limited drawing ratio of Delayed Cracking (LDR-DC) for this austenitic stainless steel.

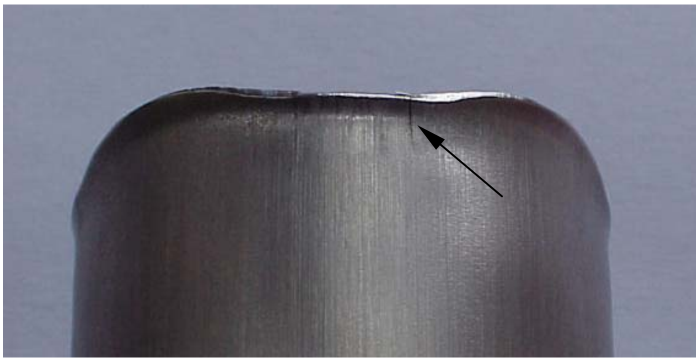


Figure 2: Delayed Cracking Phenomenon in B stainless steel.

The evolutions of the number of cracks observed in the redrawn cup edges for both austenitic stainless steels after the reedrawing are shown in Fig. 3.

As indicated in the figure, the number of cracks increased with increasing the time for B stainless steel and reached the stabilization for an 0,3 average number of cracks. On the other hand, N stainless steel hasn't spplited in cracks over the entire observing period of time, for the same drawing ratio (1.9).

As seen in the Tab. 1, the copper content present in N stainless steel is higher than in B steel and the nickel content was slightly reduced in N steel. It is stablished in the literature that Delayed Cracking Phenomenon tends to occur with steels of low nickel content (Sumitomo, 1978). This suggests that the effect of copper content was proportional to the susceptibility of Delayed Cracking, i.e., the higher the copper content, less likely became the occurrence of Delayed Cracking, even though the opposite influence of the nickel amount reduction.

3. 2. The Effect of Copper Addition on α' Martensite Variation Along the Cup Wall

Figure 4 shows the microstructure developed at various positions along the drawn and redrawn cup walls for N stainless steel. The amount of martensite obtained is seen to vary directly with the drawn cup height due to the magnitude of the radial stretching and the tangencial compression experienced by the different areas of the blank during their movement toward the cup wall. In regard to the redrawn cup, the distribution of the stresses in the deformation zone are qualitatively equal to those occurring during the first drawn. Because of the generally conical shape of the die entrance an additional normal pressure, caused by the tangencial compressive stress, presses the cup against the die (Lange, 1985). So, the entire redrawn cup wall is forced to yield into the die cavity causing further strain and, in consequence, more transformation of austenite to strain induced martensite.

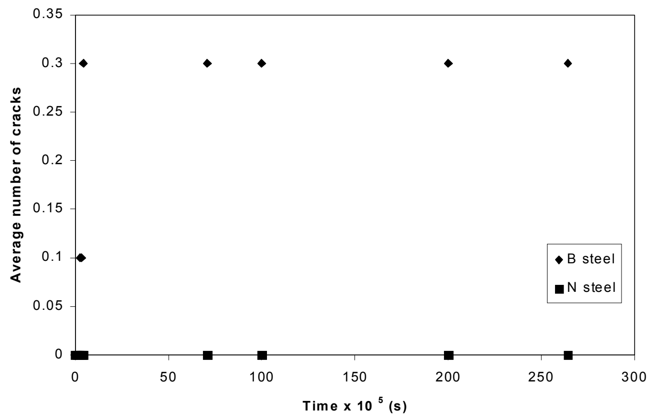
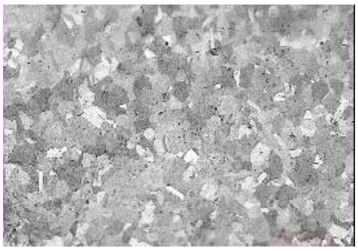
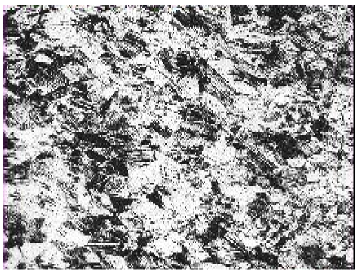


Figure 3: Susceptibility to Delayed Cracking for the B and N austenitic stainless steels.



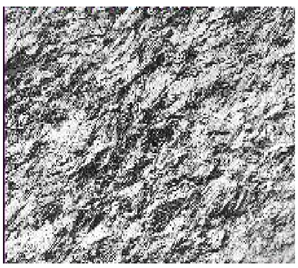
(a) N stainless steel



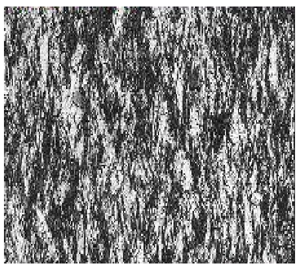
(b) drawn cup – sample 1 (base)

(c) drawn cup – sample 2 (top)

(d) redrawn cup – sample 1 (base)



(e) redrawn cup – sample 2



(f) redrawn cup – sample 3

(g) redrawn cup – sample 4 (top)

Figure 4: Optical Micrographs from strain-affected martensitic transformation in N stainless steel prior and after drawing and redrawing operations. (a) N austenitic stainless steel prior the forming, (b) base of the drawn cup, (c) top of the drawn cup, (d) base of the redrawn cup, (e) and (f) intermediate positions in the wall, (g) top edge of the redrawn cup. Magnification: 200x.

Figure 5 shows a typical X-ray diffraction profile of one B stainless steel cup wall sample. The individual diffracting planes from FCC-austenite and BCC-martensite can be clearly identified and are label in the figure. Three reflections from each phase were used to quantify phase fractions.

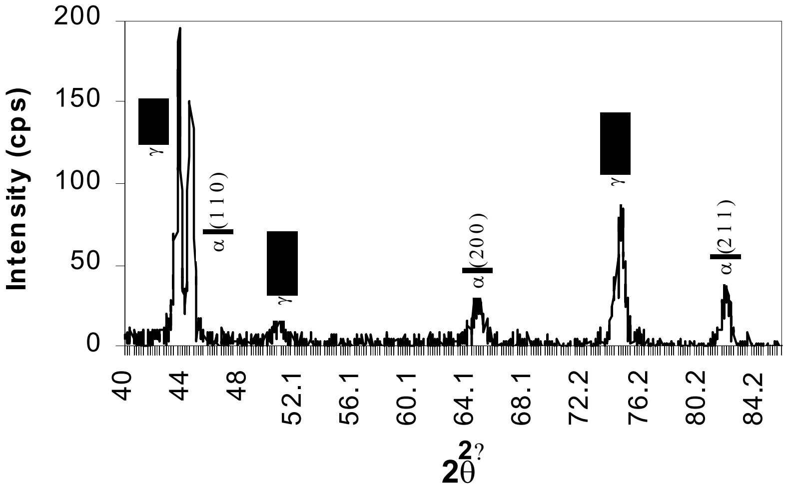


Figure 5: X-ray diffraction scan of a B stainless steel, using Cu k_{α} radiation, showing the presence of α' martensite and austenite.

The volume fractions of α' martensite in the specimens as a function of positions along the drawn and redrawn cup walls are seen in Figs. 6 and 7. It has been observed in these figures the existence of a difference in volume fraction of α' martensite through the cup walls formed in both drawing and redrawing operations. The change of the volume fraction of α' martensite as a function of the length of N redrawn cup has exihibited a linear increase, whereas B stainless steel has showed a parabolic increase behavior. However, the difference was higher in the redrawn cups of both steels. The volume fraction of strain induced α' martensite was always higher in B stainless steel for the same amount of deformation, although this tendency was clearly inverted at the base of the drawn cups.

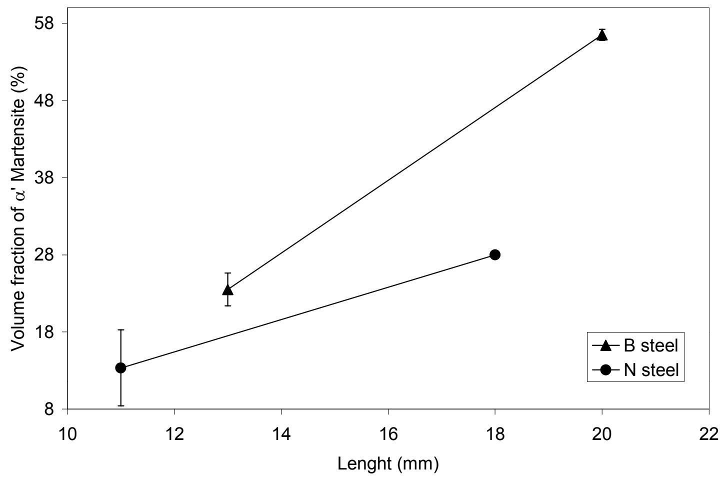


Figure 6: Change in the fraction volume of α'martensite along the length of the deep drawn cups for steels B and N.

As pointed out previously, Frehn and Bleck (2003) have reported that a gradient of α' martensite was formed in drawn cups of 301 austenitic stainless steel. They have measured up to 5% of α' martensite in the bottom areas and over 40% in the top edge. In this study, it was observed at the bottom area of the redrawn cups close to 10% of α' martensite and over 50% in the top edge of redrawn cups.

Table 2 shows the difference of the amount of strain induced martensite (Δα') formed between the base and the top of the drawn and redrawn cups for the two steels. The variation of the amount of martensitic phase in the B redrawn cup was the highest. As observed by Frehn and Bleck (2003), the Delayed Cracking Phenomenon was seen to be more likely to occur in those austenitic stainless steels (in this case, B steel) which have formed high amounts of α' martensite, over 60%, in the top edge of the cups, or have shown a high difference of this phase through the cup wall, over 35%. So, the drawn cups of both steels and N redrawn cup haven't reached any of these conditions for the crack initiation.

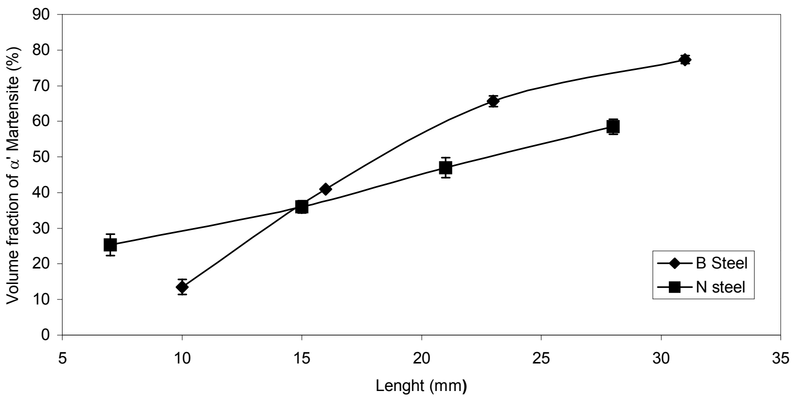


Figure 7: Change in the fraction volume of α'martensite through the walls of the redrawn cups for steels B and N.

Table 2: Variation of volume fraction of strain induced martensite (Δα') between the base and the top of the drawn and redrawn cups for B and N stainless steels.

	Δα'(%)	
Steel	**Drawn Cup**	**Redrawn Cup**
B	34	64
N	13	35

In summary, Delayed Cracking Phenomenon hasn't appear in the copper-added steel. The difference in the susceptibility to Delayed Cracking Phenomenon of the two steels can be explained in terms of the chemical composition, which has affected the stability of austenite and stacking fault energy of the steel.

The main differences in the chemical compositions of the steels are the copper content, which was added in 1.2% and nickel content, which was reduced in 0.78%. As expected, high amounts of copper have influenced the stability of the N austenite phase decreasing its Md_{30} temperature. As seen in Tab 1, Md_{30} temperature of N steel is lower than B one. This implies that N stainless steel was less prone to form martensite, as in fact was observed in this work.

In regard to the stacking fault energy, copper is known as an element for raising its value. Thus, N stainless steel can be expected to be higher stacking fault energy than B steel. Furthermore, additions of copper in AISI 304 steels have contributed to the suppression of martensite formation (Choi and Jim, 1996). So, the lower rate of formation of strain induced martensite in N stainless steel is also a direct consequence of its higher stacking fault energy.

4. Conclusions

Chemical composition affects much for the Delayed Cracking Phenomenon. The susceptibility to the phenomenon can be noticeably improved by enhancing the content of copper in austenitic stainless steel.

The amount of α'martensite formed in the steel with the lower copper content (B) has been found to be always higher than that formed in steel with higher copper level for the same strain levels. The higher the martensite content, the more likely becomes the occurrence of Delayed Cracking Phenomenon.

Copper addition in austenitic stainless steels has decreased the rate of α'martensite formation and gave rise to differences in the volume fraction of strain induced martensite through the redrawn cup walls. This result is associated with the increase in the stacking fault energy due to the addition of copper in N austenitic stainless steel

The phenomenon was associated with a high amount of α' martensite, over 60% in the top of the cups and a variation of the volume fraction of martensite between the base and the top of the redrawn cup wall over 35%.

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