

Copper based alloys hardenable by precipitation

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The paper presents the experimental research conducted with the purpose of accomplishing long products out of special copper-based alloys, from Cu-Cr-Zr systems, hardenable by precipitation, appropriate for large domains of utilization within top industries realized by modern casting – deforming procedures. Therefore, one of the modern technologic alternatives meeting these requirements is horizontal continuous casting which ensures the realization of long semi-fabricated materials out of special alloys that can be used in cast state and/or plastically deformed, in warmth and/or cold, for the accomplishment of certain products required on the market. The effect of precipitation function of hardening degree applied to the samples put in solution is quantified on consecrated compositions of the Cu-Cr-Zr alloys, containing $\approx 1\%$ Cr and $\approx 0.12\%$ Zr respectively, after the solubility treatment. The macroscopic resistance determinations as well as the electronic microscope and X-ray investigations shall furthermore lead to the accomplishment of a concluding image on the mechanism of precipitation within the analysed systems.

Key words: Copper based alloys, horizontal continuous casting.

1. Introduction

Due to their excellent electric and thermal conductivity properties, copper-based alloys are often used as materials in industries such as electro-technical, electronic, automatics, etc. (Piatti et al., 1991). From these alloys, the class of precipitation hardening alloys presents special interest for industries using top technologies, such as: oil industry (derricks); machine building industry (welding cores, pointed welding of vehicle body, etc); railroad transport (support connections, high voltage cables); nuclear industry (international experimental thermonuclear reactor – ITER) (Davis et al., 1998).

In addition to remarkable conductivity and high temperature resistance, precipitation hardening alloys also have high level of resistance to deformation, to fatigue and to small oscillations, LCF (low cycle fatigue). This excellent combination of properties determines the use of precipitation hardening alloys for the execution of state-of-the-art products: regenerative cooling rocket engines, especially for the gaskets of the main chamber (Ellis et al., 1989).

Experimental works targeted the execution of precipitation hardening alloys of Cu-Cr-Zr type by means of integrated making (melting) – continuous casting technologies.

1.1 Physical-chemical and structural characteristics

For the purpose of developing mechanical and electrical properties resulting from alloying with Cr and Zr – for the CuCrZr alloy the characteristics of pure, high purity copper (Cu>99.95%) will be presented first. Chemical composition expressed in percentages for pure, high purity copper is presented below: Cu + Ag = 99.95%; Bi = max. 0.01 %; Sb = max. 0.003 %; As = max. 0.003 %; Fe = max. 0.005 %; Ni = max. 0.002 %; Pb = max. 0.005 %; Sn = max. 0.002 %; S = max. 0.004%; Zn = max. 0.004 %; Oxygen content: <150 ppm.

Cu-Cr-Zr Chemical composition %: Cu + Ag: 99.4%; Cr 0.6-1.0%; Zr 0.05-0.15%; Impurities = max. 0.3%.

2. Experimental conditions

2.1 Defining technological parameters for HCC horizontal continuous casting

These instructions refer to the operation manner of the horizontal continuous casting installation, to the necessary adjustments, as well as the conditions for obtaining semi-finished materials made of CuCrZr precipitation hardening alloys.

2.2 Main parameters of the horizontal continuous casting

Although the continuous casting principle is simple, the procedure itself is very demanding, as the strict concordance between a large number of factors is required, starting from the casting phase to the completion of the hardening process. The most important parameters of the horizontal continuous casting which need to be correlated are:

- Temperature of the liquid alloy
Fluidity of the alloy depending on:
 - liquid-solid temperature differences
 - viscosity decreasing with the temperature and oxygen content
 - superficial tension (the smaller it is, the better it fills the die)
- Stabilization of the liquid-solid interface to approx. 0.7 L (L=length of the crystallizing vessel) and obtaining layer thickness at interface as small as possible. This matter implies the correlation of the following parameters:
 - determination of the pulling cycle
 - length of the pulling steps
 - pause times
 - pulling speeds
 - method for enforcing the pulling force
 - temperature of the cooling water
 - necessary debit
- Centring the pulling line
 - axis of the crystallization vessel with the pulling axis, cutting axis, roller's axis on the same line

2.3 Technological adjustments

Alignment of the continuous casting installation:

Alignment of the pulling device with the soaking furnace is performed by means of the following elements: crystallizing vessel, pulling primer and pulling bar. This operation is performed in cold conditions, after the crystallizing vessel has been fixed in the crucible. A bubble glass or laser alignment system is used for the alignment operation. In order to ensure straight line movement of the semi-finished material, the height and position of the support rollers will be adjusted. All rollers' position must be adjusted so that the axis of the semi-finished material corresponds perfectly to the axis of the crystallizing axis. Adjustment is performed by means of the pulling bar which has diameter equal to that of the semi-finished material and by means of the adjustment screws located on the roller's supports.

Adjusting the semi-finished material's grip vice

Depending on the size of the semi-finished material, gripping slips are installed on the device, so that the gripping throw is as small as possible. The fact that the axis of the grip vice must be on the same level as the axis of the pulling bar must be considered.

Adjustment of the oil's work pressure

Usually, the work pressure is 150 daN/cm², forbidding values of more than 250 daN/cm², depending on the dimensions of the semi-finished material.

Adjustment of the semi-finished material's pulling speed

Its value depends on the cooling capacity, the adjustment being performed by means of the baffler installed on the oil feeding pipe of the cylinder acting the pulling mass.

Adjustment of the pulling throw

Depending on technological parameters, the pulling throw is adjusted by moving the throw limiter's cam drive. Maximum throw is 80 mm.

Adjustment of the standstill time

Standstill (waiting) time of the alloy in the crystallizing vessel is obtained by means of the time relay, lasting for 3-4 seconds. The waiting times, before the pulling operation (after gripping the bar) and before the return operation, are adjusted by means of time relays and last for 2-3 seconds each.

Adjustment of the cooling water's temperature

It is performed by introducing an appropriate quantity of cold water from the network into the reclaimed water, so that the semi-finished material's temperature upon exiting the crystallizing vessel is of 300-400 °C. The water's temperature upon entering the crystallizing vessel is of 35-45 °C.

2.4 Starting the technological process

Preheating the soaking furnace:

- The induction heating installation is started. Additionally, a methane gas burner is used
- The tank is filled with water for cooling the crystallizing vessel by opening the network's water admission faucet
- The faucet on the water aspiration pipe from the tank to the pump is opened and the recirculation pump is started. The faucet allowing the admission of fresh water directly from the pump and the one used for evacuating hot water to the canal must be closed. After the installation's complete filling with water, the admission faucet from the network is closed. The water's temperature upon exiting the crystallizing vessel will be correlated to the nature of the alloy, the dimensions of the semi-finished material and the pulling speed.
- If the water's temperature exceeds the technological limit of 60-70 °C, part of the reclaimed water is evacuated, completing it with fresh water from the network. The furnace will be preheated until the moment when the crucible becomes light red and the end of the draught bar becomes dark red.

Introducing (forming) the liquid alloy in the furnace's crucible:

The temperature of the liquid crucible is a constant parameter and, usually, it is the regular casting temperature of the respective alloy: CuCrZr: 1150-1180 °C.

Before introducing the liquid alloy in the furnace's crucible, the insertion of the "pulling primer" bar in the crystallizing vessel must be verified. It is forbidden to insert liquid alloy in the crucible without installing the pulling primer bar. Protection flow and deoxidizers are introduced in the casting pot.

Casting operation:

- The installation is switched to "manual"
- Simultaneously with introducing the liquid alloy in the crucible the pulling device is started. The operator will activate the buttons from the command panel (pull, return, grip) so that, at first, the step is small and the waiting time until the exit of the pulling bar from the crystallizing vessel is minimum. When the hardened metal bar emerges, the step and the waiting time are increased until the bar becomes dark cherry to black upon exiting the graphite crystallizing vessel. From this moment the pulling installation is switched to "automatic"
- While executing the above operations, the liquid alloy feeding continues until the crucible is full. Table 1 presents the alloy's temperatures in the continuous casting of analysed precipitation hardening alloys

Table 1: Temperatures of the precipitation hardening alloys in continuous casting

Alloy	Bar diameter [mm]	Casting temperature [°C]	Bar temperature upon exiting [°C]	Cooling water entry temperature [°C]	Cooling water exit temperature [°C]
CuCrZr	60	1160	380-400	30-40	50-60
	100				
	150				

Pulling parameters of copper alloy bars are directly influenced by:

- alloy's temperature in the crucible
- cooling water temperature

- diameter of the semi-finished material
- temperature of the surrounding environment

Table 2 presents informative values of the pulling step, pulling duration and the pause duration

Table 2: Values of pulling parameters

Bar diameter [mm]	Pulling time [sec]	Pause time [sec]	Pulling step [sec]
25-40	2-5	8-12	35-60
40-55	3-6	8-13	30-40
55-70	4-7	9-13	25-35
70-85	4-7	10-13	15-30
85-100	4-8	10-14	10-25
100-150	4-8	10-14	5-15

Casting operation:

Parameters of the above table are determined by means of experiments for each diameter and type of alloy during the initial casting phase. However, the installation must be supervised continuously in two areas:

- Area where the bar exits the crystallizing vessel
- Cooling water temperature

Since the modification of the pulling step's length is more difficult (contactors' positioning), the adjustment of the pulling cycle is performed by modifying the pulling time and the pause (waiting) time. Two extreme cases can occur during operation:

- the bar is very warm upon exiting the crystallizing vessel
 - The pause time is increased
 - The area where the bar exits the crystallizing vessel is cooled with compressed air
 - The cooling water temperature upon exiting the crystallizing vessel is verified and its temperature is decreased by opening the network faucet
 - The work regime of the soaking furnace's burners is slightly reduced (in case of the soaking crucible's alloy overheating)
- the bar is cold upon exiting from the crystallizing vessel and has the tendency to block
Measures to be taken in this case are as follows:
 - Stop the pulling
 - Reduce the cooling water's debit until it can reach 70-80 °C
 - Increase the furnace's thermal regime

Cutting

It is performed by means of alternative disk saw depending on the delivery length. Note that the saw moves at the same time as the continuous cast bar.

Cooling

It is performed in the air, on the cooling bed.

Since the chemical composition of a brand allows the existence of a percentage of impurities of 1 %, when making it, deoxidation was effectuated using silica, too. In the basic matrix left a percentage of 0.63 % Si.

The study of samples was made by means of the QUANTA INSPECT F electron scan microscope provided with electron gun with field emission - FEG (Field Emission Gun) with a resolution of 1.2 nm and X-ray energy dispersive spectrometer (EDS) with resolution at MnK of 133 eV. To investigate SEM, the analysed samples were lapped and treated with chemical reactants and visualization took place at different growths.

In Figure 1 a, b, c, d is presented images of secondary electrons of a Cu-Cr-Zr sample at different growths: x1000, x2000, x4000, x8000, where are shown the granules of copper-based solid solution and compounds arranged on the deformation direction containing Cr, Zr as a majority element, but also elements such as P, Si and O₂.

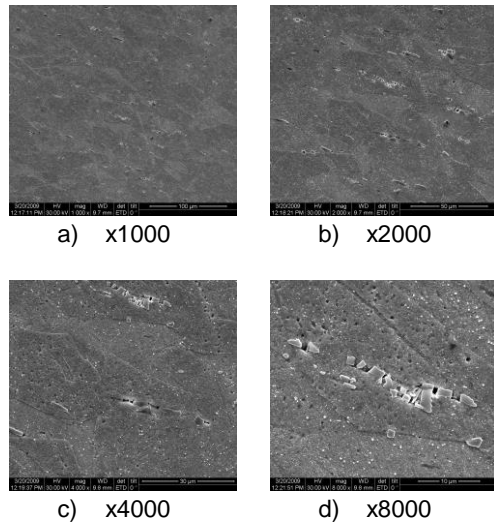


Figure 1: Microstructure of Cu-Cr-Zr sample – General aspect

Figure 2.a, b, c, d presents the images of retro scattered electrons (BSEI) on the compounds arranged on the deformation direction. Their identification was made by X-ray spectrometry.

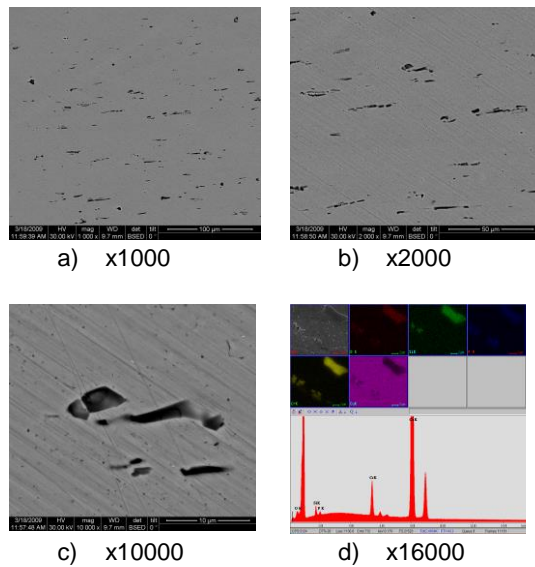


Figure 2: BSEI images on the compounds arranged on the deformation direction

There can be notice the compound with majority content of Cr, Zr, Si, P and O₂. The mechanical characteristics of Cu-Cr-Zr alloys and values around those mentioned in Table 3.

The presented values are recorded after the tempering thermal treatment, the plastic deformation and the aging thermal treatment. There can be noticed the decrease of the value of electric conductivity once with the increase of mechanical resistance as it is shown in Table 3.

Table 3: Mechanical characteristics of Cu-Cr-Zr alloys

Alloy	Tempering temperature °C	Aging time [h]	Aging temperature [°C]	Applied operations, tempering, deformation, annealing	R _m [daN/mm ²]	R _{0,2} [daN/mm ²]	A, [%]	HB
Cu-1Cr-0,12Zr	980	2	480	T+D+A	50	44	6	145

3. Conclusions

Upon commencing the continuous casting (pulling primer), the primer bar must be taken out according to the pulling regime, after maximum 60 seconds. After this time interval, if the bar remains inside the crystallizing vessel, then the hardening front moves forward to the furnace's interior, blocking the pulling process (the so called "bear shoulder" is formed after the crystallizing vessel).

If the primer bar is inside the crystallizing vessel with 20 % or 80 % of its length, then after 15 seconds, respectively 16 seconds, the pulling process can be conducted in normal circumstances. This fact confirms the possibility of situating the induction coil laterally, offering advantages related to the furnace's construction or to the operation conditions.

The crystallizing vessel must ensure the absorption of a large quantity of heat so that the temperature inside the crystallizing vessel is between decrease limits from 1800 °C to approx. 650 °C, for pulling speed of 1.2 m.

Operation parameters will be:

- water debit in the crystallizing vessel: 420 l/min
- entry temperature: 38 °C
- exit temperature: 47 °C
- water pressure: approx. 4 atm
- contact with the smelting is performed by means of graphite copper

Upon determining pulling parameters, the length of the pulling step, the pulling time and pause time, the most important physical characteristic is the thermal conductivity.

Its values influence the hardening's geometry in the crystallizing vessel. In case of high values of thermal conductivity, the hardening (liquid-solid transformation) occurs entirely inside the crystallizing vessel and commences in an area located at approx. 30% of the crystallizing vessel's length compared to the area towards the furnace.

Liquid-solid transformation surface has the shape of a spherical calotte which fills an area between 0.7-0.6 of the crystallizing vessel's length.

Pulling speeds can be small, so that the pulled bar can be hardened along the entire surface.

Once the thermal conductivity was reduced, the hardening front tends to move rapidly to the interior of the furnace, only on the surface, requiring higher and higher pulling speeds, so that the hardened surface does not form the "bear shoulder" and block the bar's pulling process.

The bar's interior is liquid and can reach up to 4-5 m from the crystallizing vessel, such distances being proportional to the reduction of the thermal conductivity.

Liquid-solid separation surface has the shape of a rotation paraboloid, its horizontal axis being larger than the horizontal axis as the alloy's conductivity becomes smaller.

Structural analysis of bars made of precipitation hardening alloys – has allowed the definition of thermal treatment and plastic deformation technological parameters offering precipitation hardening alloys the required mechanical characteristics.

Acknowledgments

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