Effect of ultrasound treatment on Cu-Zn alloys

A. Pola, L. Montesano, M. Gelfi, G.M. La Vecchia

The application of power ultrasound to liquid and solidifying alloys is known to allow the formation of a non-dendritic and fine microstructure suitable for semi-solid feedstock production. In literature several papers report results about low melting point alloys but very limited data are available on Cu-base alloys.

The aim of this paper is, therefore, to evaluate the effect of ultrasonic waves applied to Cu alloys during solidification in order to obtain a globular microstructure.

Metallographic analyses showed the effectiveness of this technique in breaking the forming dendrites, giving rise to an almost globular structure, suitable for being used in semi-solid processing.

The differences in microstructure morphology and phases composition resulted to affect the corrosion resistance of the analysed samples, in particular the semi-solid ones showed improved performance as a consequence of the homogenizing effect induced by the ultrasound treatment.

Keywords:
Copper and copper alloys, corrosion, thixoforming, materials charactization

INTRODUCTION

Pressure die-casting is conventionally used for relatively low melting point alloys (e.g., Al, Mg and Zn alloys) because of the limited die life experienced when casting higher melting materials such as Cu alloys. In this case, very severe processing conditions with temperature over 1000°C can be reached.

Semi-solid metal forming allows to work at lower temperature with subsequent increase in die life and reduction in production costs, combined with higher casting quality.

Compared to conventional forging, semi-solid processing needs higher performance materials and/or coatings for the mould [1] because of the working temperatures; however, the advantages of obtaining near net shape part, with reduced machining and finishing costs make the semi-solid technology strongly competitive [2].

Limited investigations on semi-solid die-casting of Cu base alloys have already been carried out successfully and some sample components were produced [3].

The ability to apply this technology to high melting point alloys, such as Cu, mainly depends on the development of systems suitable for producing the proper feedstock material, characterized as well known by a globular primary solid phase surrounded by the liquid phase.

Few papers are available in literature concerning different methods for preparing a globular microstructure in Cu alloys. Ward et al. started from an extruded and quenched billet; in order to assess the microstructure, small tokens were heat treated and rapidly quenched in water; microstructure analyses showed the formation of spheroids [4]. Motegi et al. investigated the use of the cooling slope method: the melt Cu alloy was poured on an inclined cooling plate where primary copper globules were generated and moved with the molten alloy into a permanent mold, maintained at isothermal holding conditions and finally quenched. As a result, fine and granular crystal structures was obtained [5]. Lim et al. used an electromagnetic stirring system to develop a semi-solid microstructure of Cu alloys. They demonstrated the influence of input frequency and stirring time on the primary solid particles size [6]; however the primary phase appears with a rosette shape even after 5 min of treatment.

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In this paper the use of ultrasound waves applied to Cu alloys during solidification was studied in order to obtain a globular microstructure.

Power ultrasounds (US) applied to liquid aluminium alloys are known to guarantee simultaneously nucleation and degassing [7-8]. Researches have been already done by several authors in order to evaluate the suitability of US method to produce semi-solid feedstock material, in the case of low melting point alloys [9-13]. However, no data are up to now available about the effect of high power ultrasound on the microstructural modification of Cu alloys.

The present research aims, therefore, at studying this technology applied to a Cu-Zn alloy, in order to evaluate the advantages and to offer an alternative to traditional methods for the production of semisolid feedstock material.

As demonstrated in the case of aluminum alloys, US treated castings show a better corrosion resistance and a higher corrosion potential, as a consequence of a more uniform solute distribution [14]. A further aim of this paper is, consequently, to assess the effect of US treatment on the corrosion resistance of the investigated Cu-Zn alloy.

MATERIALS AND EXPERIMENTAL PROCEDURES

The experiments were carried out on a silicon brass (C87500) with the addition of Mn to improve mechanical and corrosion resistance. It is a common Cu alloy for permanent mould as well as sand casting; the applications for this silicon brass ranges typically from small decorative castings to medium sized engineering components (as valves and water fittings).

The chemical composition of this alloy was determined by spectroscopy analysis, showing a content of 13 wt.% of Zn, 3.09 wt.% of Si and 1 wt.% of Mn.

The “zinc equivalent" of the alloy was predicted by the conversion equation of Guillet [15]:

$$Zn_{eq} = \frac{\%Zn + 10 \cdot \%Si + 0.5 \cdot \%Mn}{\%Cu + \%Zn + 10 \cdot \%Si + 0.5 \cdot \%Mn} \cdot 100$$

The calculated “zinc equivalent" is 35%. According to Cu-Zn binary phase diagram, this alloy should have a duplex microstructure (α and β) after peritectic solidification. Considering that the liquid alloy is poured into a small permanent die, with a consequent fast solidification and cooling rate, it is expected that a certain amount of β phase will be present in the final microstructure also at room temperature.

The melting process was experimentally studied via differential scanning calorimetric (DSC) analysis, performed with a TA Instrument Q600 apparatus equipped with Universal Analysis 2000 software. The samples were inserted into an alumina pan closed with a lid and subjected to the heating cycle in a purified argon atmosphere with a scanning rate of 10°C/min. Average liquidus and solidus temperatures were taken from 3 DSC scans. According to the findings of Birol [16], also tests at 2.5°C/min were performed in order to better assess the solid fraction versus temperature curve in a semi-solid process.

For the casting experiments, the alloy was at first melt in a laboratory furnace, by heating about 100°C above the liquidus temperature (known from previous DSC measurements) into a refractory crucible and subsequently poured into a permanent die for the manufacturing of small disks (40mm in diameter and 20 mm in height).

A second amount of liquid brass was ultrasonically treated out of the furnace in order to obtain the globular microstructure. In particular, the method used consists in applying US waves to the bath during its cooling to reach about 20% of solid fraction and subsequently poured into dies as done for the fully liquid metal. Nowadays, no ultrasound equipments suitable for this purpose are industrially available; therefore, a US device was properly manufactured, as described elsewhere [9].

After mechanical grinding and polishing, chemical etching was performed with 20 g of $(NH_4)_2S_2O_8$ in 100 ml of water for 20 seconds and metallographic investigations were carried out on samples sections in order to compare the treated and non treated alloy. A Reichert-Jung MeF3 optical microscope was used, equipped with QWin image analyser, as well as scanning electron microscope LEO EVO 40 equipped with an electron dispersive spettroscopy (EDS) probe, both in secondary electrons and backscattering way, for deeper investigation on the microstructure.

Moreover, to obtain a first evaluation of the mechanical properties of the cast samples, Rockwell B hardness test was carried out. The results were the mean values of at least 10 measurements per sample, to guarantee a good statistic.

Electrochemical corrosion tests were finally performed on square section specimens ($1cm^2$) machined from the cast disks, in a 3.5%wt sodium chloride aqueous solution at room temperature. The AMEL 7050 potentiostat used for the polarization experiments was set in the 3 electrodes standard configuration: platinum counter electrode (CE), saturated calomel reference electrode (SCE) and working electrode (WE). The polarization curves were collected, after 30 minutes of immersion into the solution, by stepping the potential at a scan rate of 0.5mV/s from -500mV to +800mV respect to SCE. Using an automatic data acquisition system, the potentiodynamic polarization curves were plotted and both corrosion rate and potential were estimated by the Tafel extrapolation method and primary passivation potential and current were extrapolated from the curves. A minimum of 3 tests were performed both for treated and non treated casting samples.

RESULTS

A copper alloy for semi-solid application must have an appreciable melting range, so that it is possible to obtain globules of α-phase in the solidification range.

The DSC curves (Fig. 1) show the solidus temperature at about 836°C (first exothermic peak) and the liquidus around 935°C (second exothermic peak) for both the heating rate used. The results are in good agreement with the literature data for this brass (820 and 917 °C) [ASTM B198-13B]; in particular, the measured temperatures are slightly higher, probably because the Zn content corresponds to the lower limit of the range defined in the standard.

Solid/liquid fraction at the forming temperature is an important parameter in semi-solid processing as it affects the slurry viscosity and the subsequent mould filling. It can be calculated from the DSC, assuming that the amount of latent heat evolution is directly proportional to the liquid fraction which is equal to 1 at full melting; therefore, liquid fraction is obtained by integrating the DSC signal between the liquidus and solidus temperatures.

The result is shown in Fig.1b and it indicates that the most suitable temperature range in which to thixoform is 895-920°C, where the solid fraction is between 15-55%.

According to these results, the alloy was US treated for 40 sec, down to 915°C in order to reach about 20% of solid fraction.

The effect of the ultrasonic treatment (UST sample) compared to the conventional casting (NUST sample) is shown in Figure 2. As expected, the microstructure is composed by α and β phases. NUST samples show the presence of fine primary α-phase columnar dendrites with an average SDAS of 24 μm, surrounded by a certain amount of interdendritic β-phases.

Differently, in the case of the UST sample, the primary α-phase has a globular shape. Therefore, the ultrasonic treatment results effective in breaking the dendritic microstructure, giving rise to

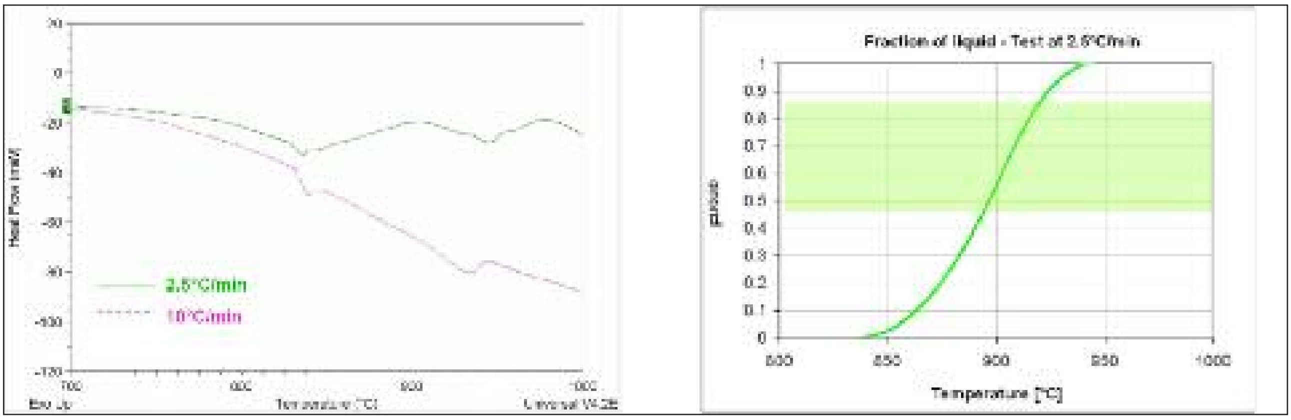


FIG. 1 ***DSC curves and liquid fraction vs. temperature.***

Curve DSC e frazione di liquido al variare della temperatura.

FIG. 2
Microstructures of NUST (a) and UST sample (b).
Microstruttura dei campioni: (a) non trattati US e (b) trattati con US.

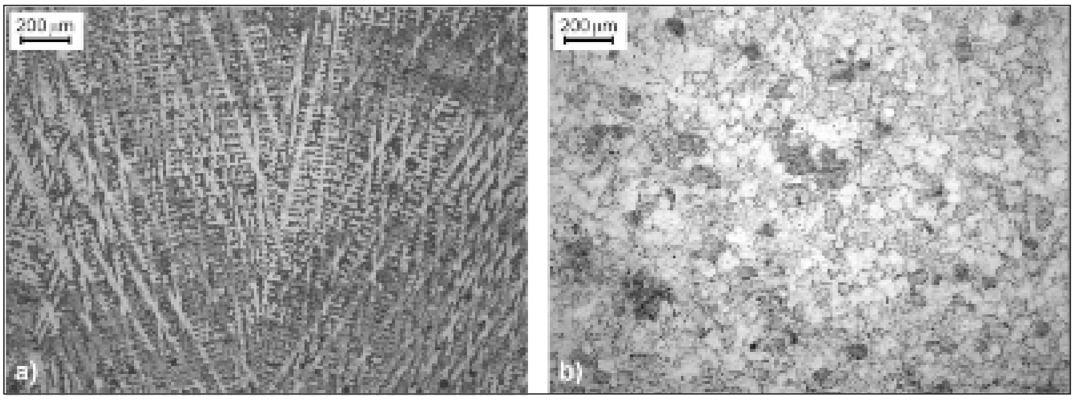
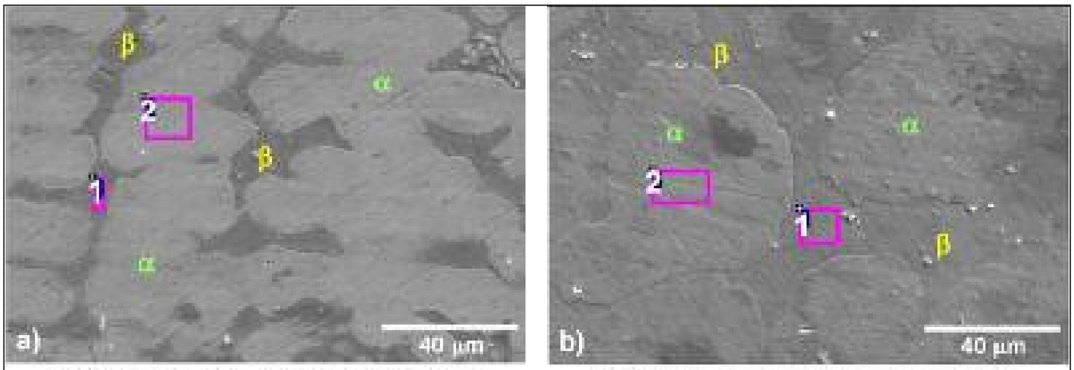


FIG. 3
SEM analyses: microstructure and EDS spectra in wt. % of NUST (a) and UST sample (b).
Analisi SEM: microstruttura e spettri EDS in peso % dei campioni NUST (a) e UST (b).



Spectrum	Si	Mn	Cu	Zn
1	5.92	1.99	80.95	11.14
2	2.20	0.34	84.31	13.16

Spectrum	Si	Mn	Cu	Zn
1	4.93	1.82	82.35	11.10
2	2.04	0.39	84.01	13.56

an almost globular structure. Globules are uniformly distributed and they present an average size of 65 µm and a shape factor of 0.65. It is important to remark that the rheological behavior in the semi-solid state strongly depends on the solid phase shape factor [17-18].

In Fig. 3 two microstructures obtained by scanning electron microscope at high magnification are shown.

Considering the UST sample, no liquid phase appears entrapped into the globules therefore it fully contributes to the lubrication of the relative movement of the solid phase particles [19]. EDS semi-quantitative analyses on α and β phases show the higher content of β stabilizing elements, such as Si and Mn, in the interdendritic/interglobular areas. It must be noticed that the NUST β-phase is richer of these elements and poorer in Cu than the UST one, probably as a consequence of different solidification conditions induced by the application of the ultrasonic waves. The difference in chemical composition of the β-phase can also explain the higher resistance of the UST sample to the metallographic etching.

Rockwell B measurements show a little higher values in the case NUST samples than the UST ones (62 ±4 HRB vs. 58±4 HRB). This result can be related to the higher content of Si and Mn measured in the β-phase of the NUST sample that makes it harder.

The differences in microstructure morphology and phases composition induce important effects on corrosion properties of UST and NUST samples, as can be observed in the electrochemical polarization curves obtained for both conditions (Fig. 4). The E-i curves have a similar trend, but the NUST curve is shifted at higher current densities, pointing out the lower corrosion resistance of NUST samples than the UST ones. In particular, for the NUST samples the mean corrosion current density (i_{corr}) calculated by means of the Tafel method is equal to 6.7±1.6 µA/cm^2, while for the treated alloy i_{corr} is only 1.7±0.5 µA/cm^2. The corrosion potential is in between -0.23 and -0.24 V, in agreement with literature [20].

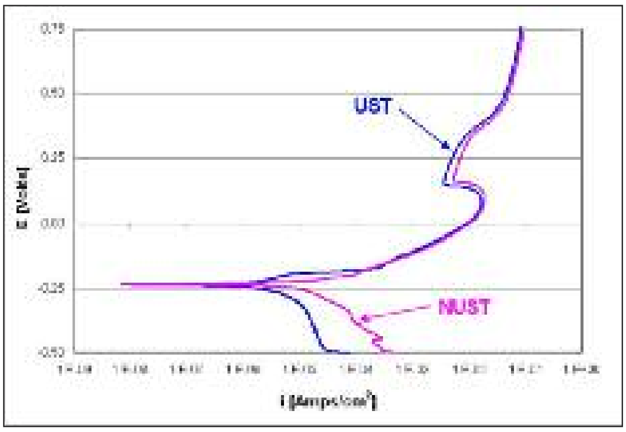


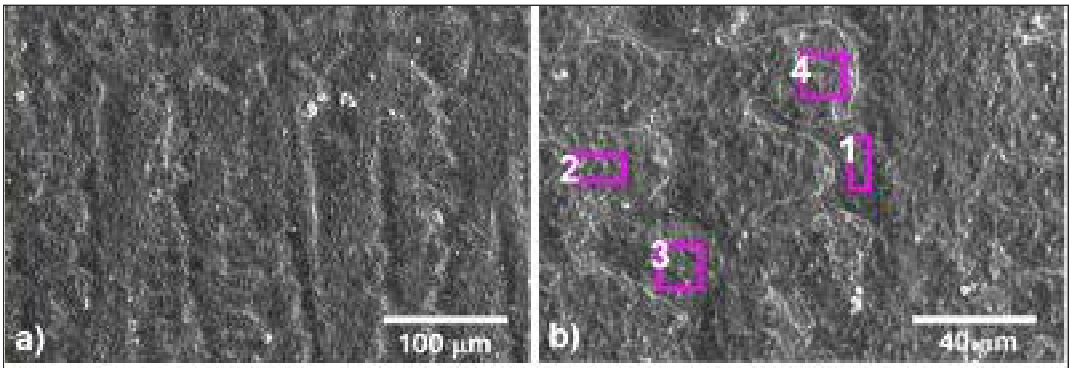
FIG. 4 ***Polarization curves for NUST and UST samples.***
Curve di polarizzazione per i campioni NUST e UST.

To explain the better corrosion behaviour of UST samples it must be considered the corrosion mechanism in a duplex brass microstructure. In this case, β is the most corrodible phase because of its lower content of Cu, that is the noblest element in the alloy [21]. For this reason, in general, β is anodic to α-phase and it preferentially dissolves in the solution.

Considering the EDS results reported in Fig. 3, it is evident that the β-phase in the UST samples has a lower content of Si, Mn

FIG. 5 ***SEM analyses on the corroded NUST samples surface.***

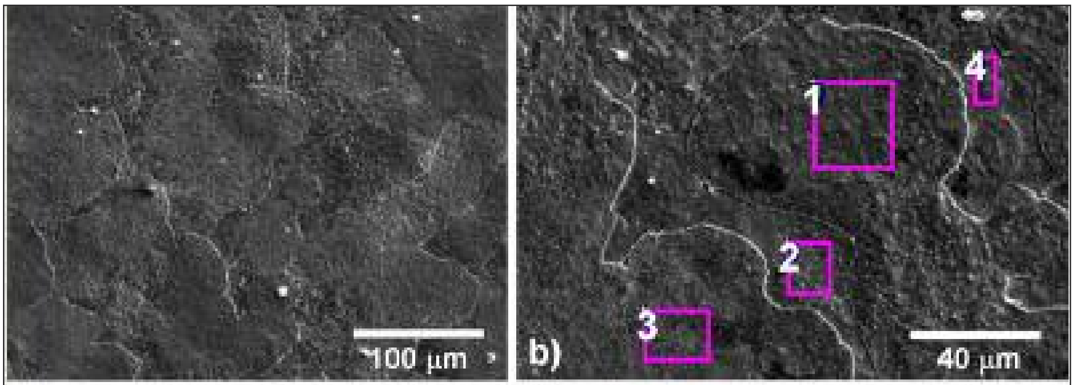
Analisi SEM della superficie corrosa del campione NUST.



Spectrum	O	Si	Cl	Mn	Cu	Zn
1	1.18	5.35	0.30	1.67	80.36	11.13
2		2.07		0.52	83.25	14.15
3	2.99	6.44	0.46	2.32	77.34	10.44
4		2.62		0.80	83.47	13.32

FIG. 6 ***SEM analyses on the corroded UST samples surface.***

Analisi SEMM della superficie corrosa del campione UST.



Spectrum	O	Si	Cl	Mn	Cu	Zn
1	0.66	2.06		0.67	83.59	13.02
2	1.61	5.55		1.25	80.05	11.54
3	1.09	2.43	0.54	0.57	81.64	13.72
4	1.60	5.04	0.39	1.41	80.03	11.53

and Zn and an higher content of Cu than the NUST ones. The reduced compositional difference between α and β phases decreases the microgalvanic effects and the consequent selective corrosion. Moreover, the UST globular microstructure compared to the dendritic one has a lower number of interfaces α/β, i.e. a lower number of preferential corrosion sites. These observations were confirmed by SEM-EDS analyses performed on the samples surfaces after polarization tests (Fig 5-6). It is evident in both NUST and UST samples that β phase is more corroded than α phase. In particular, in the NUST samples the β areas are deeper corroded than in the UST ones because of the greater difference in Cu content between α and β, as above mentioned and here confirmed by the analyses.

In conclusion, the better corrosion resistance of UST alloy can be related to the homogenizing effect of ultrasound treatment and to the formation of a more suitable microstructure.

CONCLUSIONS

In this paper the effect of ultrasound applied to Cu alloys during solidification, down to about 20% of solid fraction, was investigated in order to obtain microstructure suitable for semi-solid processing.

Metallographic analyses showed the effectiveness of this technique in breaking growing dendrites and in forming a globular structure. EDS investigations revealed also a different content of stabilizing elements, such as Si and Mn, in the interdendritic/interglobular areas as a consequence of the different solidification conditions induced by the application of the ultrasonic waves.

Corrosion tests showed a higher corrosion resistance of the UST samples as a consequence of the chemical homogenization due to the ultrasound treatment. In fact, the β areas of the NUST samples were deeper corroded than those of the UST ones because of the greater difference in Cu content between α and β.

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Abstract

Effetto del trattamento ad ultrasuoni di leghe Cu-Zn

Parole chiave: Rame e leghe, corrosione, thixoformatura, caratterizzazione materiali

Il processo di pressocolata è principalmente utilizzato per la produzione di getti in leghe a basso punto di fusione (come le leghe base Al, Mg e Zn), mentre è meno usato nel caso di leghe altofondenti (es. base Cu) a causa delle elevate temperature di esercizio che riducono la durata degli stampi.

In quest'ottica l'impiego di una lega di Cu allo stato semi-solido rappresenterebbe un indubbio vantaggio, se paragonato ad una colata convenzionale, dal momento che permetterebbe di lavorare a temperature più basse, allungando la vita utile delle attrezzature e migliorando la qualità dei getti.

Rispetto ad un processo di forgiatura, invece, lo stampaggio in semi-solido richiede temperature di lavoro maggiori e comporta la necessità di utilizzare stampi più performanti o ricoperti con rivestimenti ceramici. Tuttavia, la possibilità di ottenere pezzi near-net-shape, con ridotte lavorazioni meccaniche ed operazioni di finitura, rendono tale tecnologia particolarmente vantaggiosa e competitiva.

Da ormai 30 anni si studiano i vantaggi del semi-solido delle leghe di alluminio e più recentemente anche degli acciai. Pochi studi sono stati invece condotti sull'utilizzo di questa tecnologia per produrre componenti in lega di Cu. La ragione di questo scarso interesse va ricercata principalmente nella difficoltà di sviluppare un sistema adatto per produrre il materiale di partenza con una struttura caratterizzata da globuli di fase primaria circondati dal liquido.

Obiettivo del presente lavoro è quello di valutare l'effetto dell'applicazione di onde ultrasonore a leghe di Cu-Zn in fase di solidificazione, al fine di ottenere una struttura non dendritica adatta per i processi in semi-solido.

A tale scopo sono state effettuate alcune prove sperimentali su una lega C87500 trattata ad ultrasuoni fino al raggiungimento del 20% di fase solida. I campioni così ottenuti sono stati sottoposti ad indagine metallografica, che ha permesso di dimostrare l'efficacia del trattamento al fine di ottenere una struttura globulare.

Le analisi EDS hanno rivelato un diverso contenuto di elementi stabilizzanti (Si e Mn) nelle zone interdendritiche dei getti tradizionali rispetto a quello riscontrato nelle zone interglobulari dei getti in semi-solido, a seguito delle diverse condizioni di solidificazione indotte dall'uso di onde ultrasonore.

Le differenze di microstruttura e di composizione chimica delle fasi influenzano la resistenza a corrosione dei campioni, come hanno dimostrato le prove di polarizzazione elettrochimica effettuate con un potenziostato in configurazione standard a tre elettrodi. In particolare, il campione con struttura globulare è risultato più resistente a seguito dell'omogeneizzazione indotta dal trattamento ad ultrasuoni.