Experimental investigation of ageing in Al-Si-Cu-Mg-Ag cast alloys

A. Pola, R. Roberti, B. Rivolta, G. Silva, R. Gerosa

Manufacturing components in light metals is becoming fundamental as well as replacing higher density materials with aluminium alloys. However, whereas productions by forging and pressing can use well-known materials (i.e. 6000, 2000 and 7000 series), thixoforming and rheoforming just employ a limited number of foundry alloys (A356 and A357), which need T4, T5, or T6 heat treatments to improve their mechanical performances, fairly modest compared with those of wrought alloys. These properties can be increased by modifying alloy composition, i.e. adding new elements and/or differently balancing those already present, and consequently inducing different behaviours to heat treatment.

Keywords:
DSC, dilatometer, precipitates, activation energy

INTRODUCTION

Over the years, a family of process routes and process alternatives for semi-solid forming have been developed and industrialized [1]. One of the alternative method used for slurry preparation is the ultrasound technique, according with high-power ultrasonic vibrations are introduced into a liquid alloy, leading to cavitation and acoustic streaming. Cavitation involves the formation, growth, pulsation and collapse of bubbles, generating high impact forces; consequently, these hydraulic shock waves fragment the rising crystals, by breaking dendritic structures, increasing the nucleation centres [2]. At the same time, acoustic streams induces a vigorous stirring of the bath, homogenizing the alloy. Moreover, cavitations phenomena originate also a rapid development of hydrogen bubbles, causing their following coalescence and flotation on the liquid metal surface and, therefore, promoting the alloy degassing [3, 4].
Therefore, castings obtained by treating the alloy in the liquid/semi-liquid state by ultrasound (US) offer improved performances [5, 6].
Where high strength and low weight are required, as for instance in the case of automotive parts, further increase in mechanical properties must be achieved by using heat-treatable, i.e. precipitation-hardening, aluminum alloys.
In this experimental work an Al-Si-Cu-Mg-Ag cast alloy, suitable for semi-solid applications, was investigated in order to identify the best solution and ageing temperatures and to better understand its precipitation hardening behaviour. The technical literature states that, in these alloys, the strengthening effect is given by different types of precipitates: as binary precipitates, i.e. ($CuAl_2$) or (Mg_2Si); ternary precipitates as S ($CuMgAl_2$) or quaternary as Q ($Al_5Cu_2Mg_8Si_6$), one containing Cu and Al and one containing Ag (Ω type, with a composition close to $CuAl_2$) [7-10]. The tetragonal Ω phase is particularly advantageous because, by precipitating as plates in high densities on {111}Al planes, it promotes a higher yield strength by interacting more strongly with glide dislocations than ’ [11]. Because of the high cost, Ag has limited applications in certain Al premium-strength alloys [12]; for the same reason no binary Al-Ag alloys are in use, but small addition (0.1-06%) are effective in improving mechanical properties in some AlCu and AlZnMg alloys [13]. These alloys only recently became commercially available and other different chemical compositions are still under development, mainly addressed to the aerospace and automotive industry.
In this research, even though Cu:Mg ratio is not high, silver was added to an AlSi alloy, together with small percentage of other precipitation hardening elements (Cu, Mg), in order to evaluate the response to heat treatment in two different cases, that is in castings characterized by dendritic rather than globular microstructure.
Therefore, small amount of the alloy was produced and some of the available heats were treated by ultrasonic technique, in order to obtain a globular microstructure, as in the case of semisolid castings. Metallurgical investigations were performed on both the samples (semisolid and conventional castings) to assess ageing effectiveness.
In particular, the ageing temperatures were studied by dilatometric and calorimetric techniques varying the solution temperature (510°C and 540°C); according to the observed results, three ageing temperatures were investigated and some hardness profiles were obtained varying the soaking times.

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MATERIALS AND EXPERIMENTAL PROCEDURES

The experiments were carried out on a hypoeutectic Al-Si alloy, produced from commercially pure elements with the addition of precipitation hardening elements. According to spectroscopy analysis, the resulting chemical composition was as in Table 1.
The liquidus and the eutectic temperatures were measured by means of differential scanning calorimetry (DSC) analysis, performed with a TA Instrument Q600 apparatus equipped with

Si [%]	Cu [%]	Mg [%]	Ag [%]	Al [%]
5.50	0.33	0.44	1.00	Bal.

Tab. 1 Chemical composition of the investigated alloy.
Composizione chimica della lega oggetto d'indagine.

Universal Analysis 2000 software. All the DSC analyses were carried out in a purified argon atmosphere with a scanning rate of 10°C/min; the liquidus and eutectic temperatures resulted equal to 620°C and 562°C respectively.

The alloy was obtained according to the following procedure:

1. about 1 kg of alloy was melt in a refractory crucible, 30-40°C above the liquidus temperature,
2. about 0.5 kg of alloy was cast into a laboratory gravity die to produce small disks (Ø=40 mm, H=15 mm). These samples were named not US treated or as-cast;
3. the remaining liquid was treated by US for 90s and subsequently poured into the same laboratory gravity dies used for the as-cast alloy. These new samples were named US treated.

The heat treatment analysis involved both the solution and the ageing temperatures: according with the measured eutectic temperature, two solution temperatures were selected (510°C and 540°C); in particular, the solution conditions were 510°C-4 hours, followed by water cooling, and 540°C-4 hours with subsequent water cooling.

The ageing parameters were firstly investigated by dilatometric and calorimetric tests, using respectively a NETSCH 402 ES dilatometer and a TA instruments Q600 calorimeter, equipped with Universal Analysis 2000 software. The ageing temperatures were studied with dilatometric non-isothermal technique using two heating rates (2K/min and 5K/min), while for calorimetric non-isothermal analyses four heating rates were selected (2K/min, 5K/min, 10K/min and 20K/min).

The comparison between the dilatometric and calorimetric results suggested a further investigation at ageing temperatures of 180°C, 200°C and 220°C.

Finally, Vickers hardness profiles of as-solutioned (at 510°C and 540°C) and as-aged (at 180°C, 200°C and 220°C) samples were obtained varying the ageing times.

RESULTS

From a microstructural point of view, the effect of the ultrasonic treatment is shown in Figure 1.

The as-cast samples show a dendritic microstructure, typical of foundry products (Figure 1a). Concerning the US treated sample (Figure 1b), the ultrasonic treatment was effective in breaking the dendritic microstructure, giving rise to an almost globular structure that, in the technical literature, is usually associated with better mechanical properties [5, 6]. Nevertheless, on the other hand, the as-cast microstructure resulted slightly finer.

In Figure 2 the microstructure of the samples after heat treatment are shown, as an example in the case of solution at 510°C-4hours, followed by quenching and ageing at 180°C-2hours. In the not US alloy dendrites can be detected. In both cases, the eutectic is characterized by silicon particles having rounded and agglomerated morphology as a consequence of the solution heat treatment.

The DSC analyses, performed at different heating rate, showed similar results for the as-quenched non US and US treated samples, as shown in Figure 3 for the specific case of 5 K/min heating rate. In all the experimented conditions, the reactions were gradually shifted to higher temperature range as increasing the heating rate, indicating that these reactions are thermally activated processes.

The Kissinger approach for the calorimetric data allows to calculate the activation energy varying the heating rate according to equation (1):

$$\ln\left(\frac{\beta}{T_p^2}\right) = \frac{-Q}{RT_p} + C \qquad (1)$$

whereas:

β =heating rate [K/min]

Q = activation energy [kJ/mole]

R = 8.31 J/molK

T_p=onset temperature of the considered peaks [K]

C= constant

Concerning the first exothermic peak (GP zone – Figure 3), whose temperature is between 60-90°C for both US and as-cast samples, the activation energy resulted about 34-37 KJ/mol; according to the literature [14-15], it is very close to the energy needed for the migration of Cu atoms to cover lattice vacancies and for the formation of the GP zones.

The peak A has a characteristic temperature close to 180-220°C and an activation energy of 68 KJ/mol; this can be associated to the formation of ” or ” phase that, according to literature, needs an energy of 72 kJ/mol [16] and 75 kJ/mol [17] respectively.

Finally, the peak B takes place between 240-270°C and its activation energy is about 89 kJ/mol. This step in the ageing process is associated with the formation of S' (precursor of ternary S precipitate) or Q' (precursor of quaternary Q precipitate) [18]. Stable phases are expected to form at higher temperatures.

Being the calorimetric results very similar for US and non-US treated samples in all the performed experiments, some non-isothermal dilatometric tests [19] were further performed only on the US material. In Figure 4 the results for samples solutioned

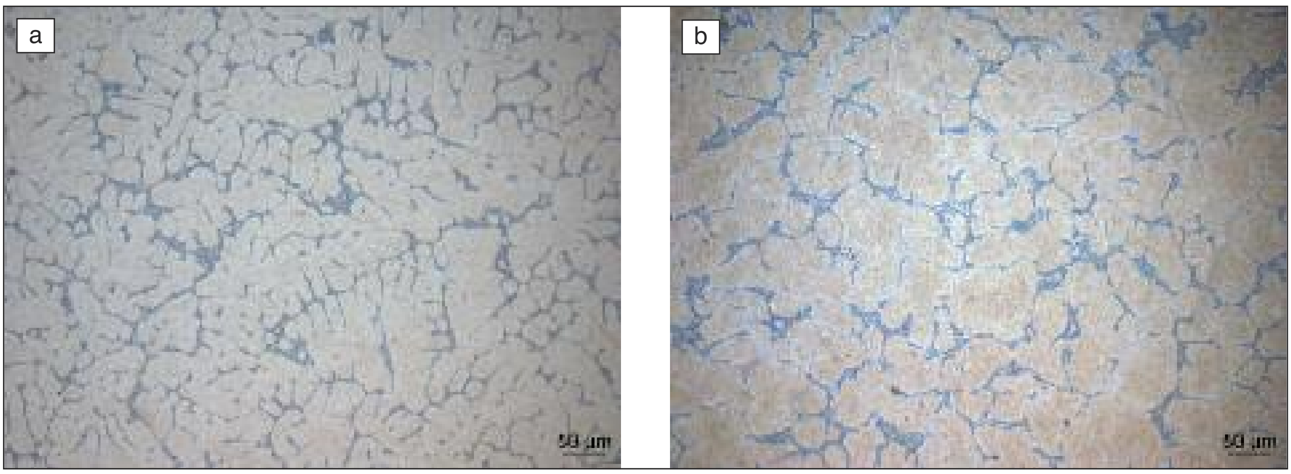

FIG. 1 ***Microstructures observed in the as-cast (a) and in the US treated as-cast (b) material.***

Microstruttura osservata nel campione as-cast (a) e in quello trattato US (b).

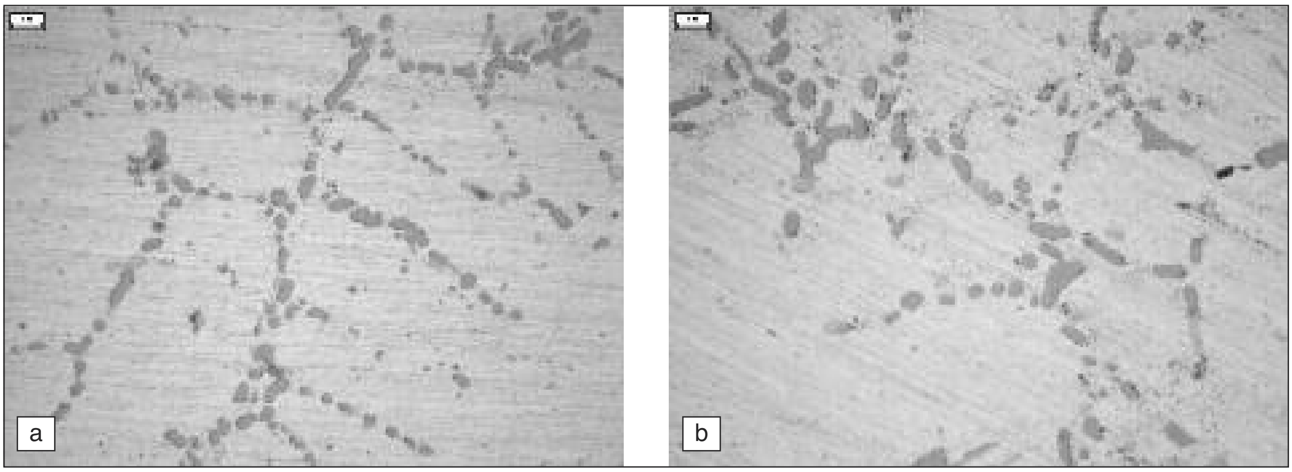

FIG. 2 ***Microstructures observed in the as-cast (a) and in the US treated as-cast material (b) after heat treatment (solution at 510°C-4hours and ageing at 180°C-2hours).***

Microstruttura osservata nel campione as-cast (a) e in quello trattato US (b) dopo trattamento termico (solubilizzazione a 510°C-4ore e invecchiamento a 180°C-2ore).

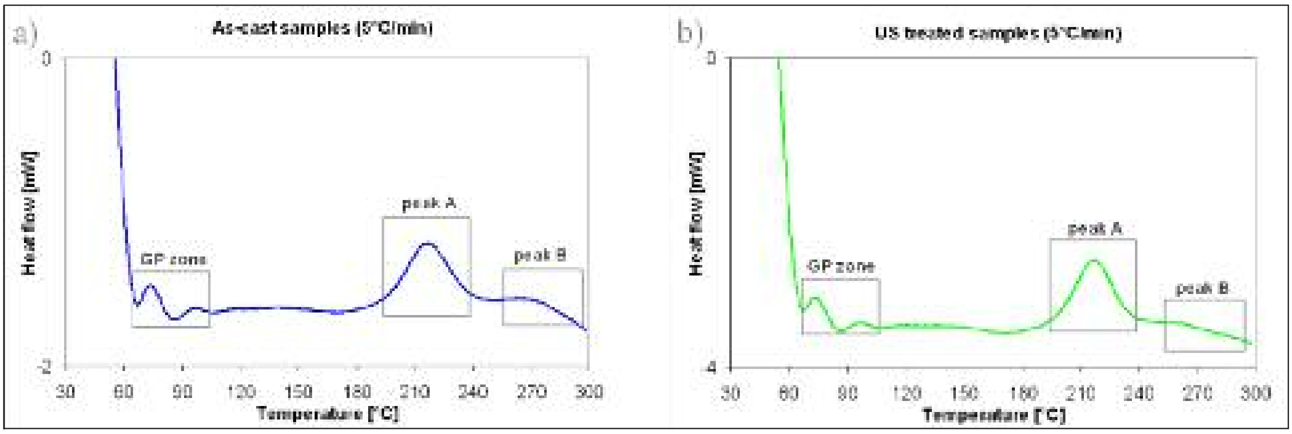

FIG. 3 ***DSC curves for as-cast (a) and US treated (b) samples, heating rate of 5 K/min.***

Curve DSC per i campioni as-cast (a) trattati US (b), velocità di riscaldo di 5 K/min."

at 510°C-4hours and heated at 5K/min, are reported to allow a comparison with those obtained by DSC analysis. As shown, a similar ageing temperatures range was identified at about 190°C - 230°C (peak A).

The ageing kinetics was hence studied by hardness tests (HV10) on small specimens (10mm x 10mm x 10mm) at temperatures of 180°C, 200°C and 220°C. The solution was carried out at both 510°C and 540°C, 4 hours, followed by water cooling. In Figure 5 and 6 the hardness profiles are reported for the as-cast and the ultrasound treated samples.

The previous results show that the ageing temperature was very effective in increasing the precipitation rates, even if the temperature of 220°C resulted in a over-ageing soon after the hardness peak. On the other hand, nor the solution temperature neither the ageing temperature affected the hardness peak/steady state notably. It's hence possible to state that the lower solution temperature (510°C) should be preferred, because from an industrial point of view the higher one could result in a partial melting being the temperature of 540°C quite close to the eutectic temperature.

For this reason, a further analysis was carried out on samples solutioned at 510°C, aiming to calculate the activation energy of both the as-cast and the US treated samples. The activation energies were calculated using both the DSC and the hardness data

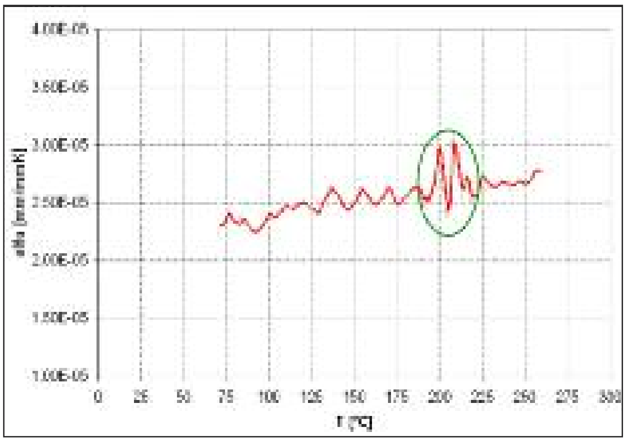

FIG. 4 ***Dilatometric curves at heating rate of 5K/min.***

Curva dilatometrica con velocità di riscaldo di 5 K/min.

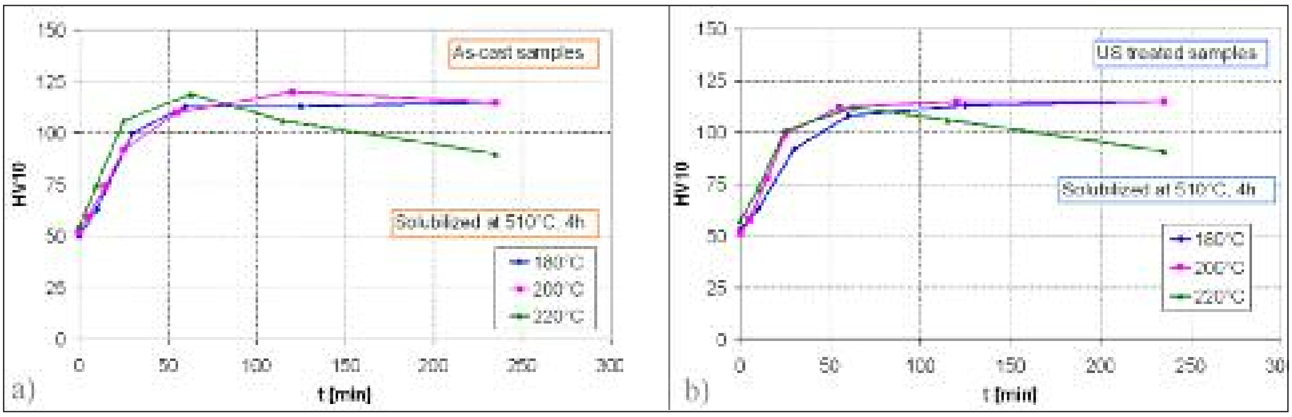

FIG. 5 ***Hardness profiles varying the ageing temperatures for samples solutioned at 510°C, 4h.***
Profili di durezza al variare della temperature di invecchiamento per campioni solubilizzati a 510°C, 4h.

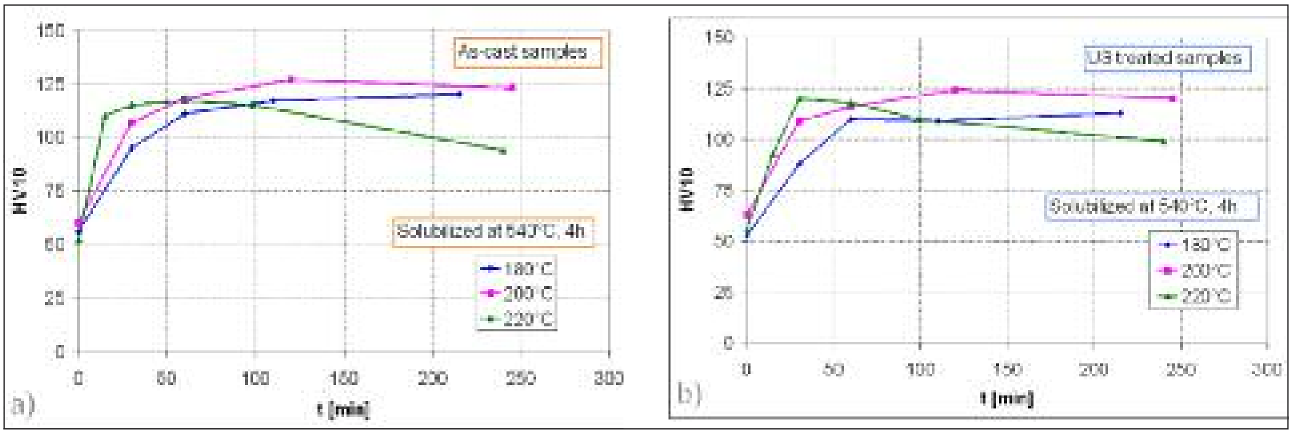

FIG. 6 ***Hardness profiles varying the ageing temperatures for samples solutioned at 540°C, 4h.***
Profili di durezza al variare della temperature di invecchiamento per campioni solubilizzati a 540°C, 4h.

as widely described in the technical literature [20-23]. The Arrhenius equation, in fact, relates the precipitation rate with the temperature as follows:

$$v = A \cdot e^{\left(\frac{-Q}{RT}\right)} \qquad (2)$$

v = reaction rate
A = pre-exponential factor
Q = activation energy [kJ/mole]
R = 8.31 J/molK
T = temperature [K]
As mentioned before, the Kissinger approach for the calorimetric data allows to calculate the activation energy varying the heating rate according to equation (1). The activation energy can be calculated using the hardness data too; in this case the reaction rate is evaluated as:

$$v = \frac{dH}{dt} \qquad (3)$$

H=hardness value (in our tests we employed the Vickers scale)
t= time [min]
The activation energies calculated with both the procedures in the case of the peaks in the range 180°C – 220°C, showed a good agreement as reported in Table 2.

DSC		Hardness	
as-cast [kJ/mole]	US treated [kJ/mole]	as-cast [kJ/mole]	US treated [kJ/mole]
68.0	67.9	65.3	72.2

TAB. 2 ***Comparison between the activation energies calculated by DSC and hardness data.***
Confronto fra l'energia di attivazione calcolata mediante DSC e attraverso i dati di durezza.

CONCLUSIONS
In the present paper a comparison between the response to heat treatment of a drop-cast and of an ultrasound treated and drop-cast Al-Cu-Mg-Ag alloy was carried out. The experimental tests led the authors to the following conclusions:
- the ultrasonic treatment in liquid phase influenced the structure morphology of the alloy, passing from a dendritic to a globular microstructure;
- the dilatometric and calorimetric tests allowed the identification of a range of ageing temperatures in which the strengthening precipitations occur similarly in both as-cast and US treated alloys;
- the solution temperature, within the limits of this investigation, doesn't affect the hardness peak after ageing notably;
- the precipitation kinetics speeded up as the ageing temperature increased, but after 200°C an over-ageing occurs very quickly;
- the most interesting ageing temperature was estimated to be 200°C, because a hardness steady state is reached in about 2

hours and no over-ageing occurred up to 4 hours;

- the activation energies calculated using DSC and hardness data are comparable and they are very close for the as-cast and the ultrasound treated samples;
- higher temperatures are needed to complete the ageing kinetics with subsequent formation of the Q, or Ω stable phases.

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Abstract

Studio sperimentale dell'invecchiamento di leghe Al-Si-Cu-Mg-Ag da fonderia

Parole chiave: alluminio e leghe, precipitazione, fonderia, caratterizzazione materiali

Il processo di pressocolata delle leghe metalliche allo stato semisolido è considerato particolarmente promettente in quanto consente di fabbricare parti di geometria complessa, in forma quasi finita, suscettibili di trattamento termico di tempra di soluzione ed invecchiamento, dal momento che il getto ottenuto con questa tecnologia è pressoché esente da porosità da gas.

I componenti attualmente pressocolati in semisolido vengono fabbricati con leghe Al-Si convenzionali quali la A356 (Al7Si0.3Mg); le proprietà meccaniche di tali manufatti, pur essendo superiori a quelle dei getti ottenuti per colata tradizionale, sono inferiori a quelle di componenti analoghi fabbricati per fucinatura con leghe di alluminio da deformazione.

Precedenti studi hanno permesso di individuare una lega di alluminio, idonea alla colata in semisolido, contenente piccole percentuali di elementi alliganti, quali Mg, Cu ed Ag che, in presenza del Si, offrono ottime potenzialità di indurimento per precipitazione a seguito di trattamento termico di tempra di soluzione seguita da invecchiamento.

Scopo del presente lavoro è quello di individuare le condizioni di trattamento ottimali, definendo la cinetica di precipitazione delle fasi indurenti, al fine di migliorare le prestazioni del manufatto.

La lega è stata pertanto soggetta ad una serie di test di solubilizzazione ed invecchiamento artificiale, combinando diverse temperature e durate; per valutare l'efficacia del trattamento T6 si sono eseguite prove di microdurezza HV.

Parallelamente, è stata studiata la cinetica di decomposizione della soluzione solida sovrassatura mediante analisi comparative condotte con il dilatometro e con il calorimetro a scansione differenziale al fine di individuare l'intervallo di temperature entro cui avvengono le trasformazioni.

Lo studio delle curve flusso termico-temperatura, ottenute con il DSC a differenti velocità di riscaldo, ha permesso d'identificare una serie di picchi di flusso termico attribuibili alla precipitazione di fasi indurenti; questo è stato possibile confrontando la loro energia di attivazione caratteristica (ricavabile dall'equazione di Kissinger) con i valori tipici reperibili in letteratura.