Investigations on the effect of low temperature cooling on the phase transformations of the EN AW 7075 alloy

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Abstract. Al-based alloys are very challenging materials, especially in applications where energy and mass reduction are required. In this scenario, EN AW 7075 Al-based alloy can be considered of high interest for different large and thick products. One of the many fields of interest where large geometry dynamic is present is, for example, aerospace, where the alloy structural stability in different conditions is very important. In this paper, the main attention is oriented toward the structural investigation of the EN AW 7075 Al-based alloy in different condition, by differential scanning calorimeter and dilatometry analysis, in order to be able to propose it, as a suitable material for aerospace component production. The analysis on the conditioned and un-conditioned materials has been used to assess the alloy’s performance and to control the evolution of the alloy properties, in specific conditions, important aspect for the targeted application. Some data on the mechanical behaviour of the alloy integrate the study.

1. Introduction
A precipitation-hardened, high-strength, good wear and corrosion resistance EN AW 7075 Al-based alloy [1-3], is remarkable material and it is used in different critical engineering applications, like automotive and aeronautical domain. In such area, the alloy has to show high plasticity, lightweight, excellent aesthetic features, high mechanical properties combined with high production rate and stress-free assemblage. Additionally, it is important to have a material which can withstand and able to maintain identical properties also in severe environment or risky conditions, like high pressure, high or low temperature, presence of chemically harmful medium, etc. [4, 5]. Localized corrosion, because of its chemical composition, is common in such alloys. In particular, the presence of many different constituents defines the heterogeneity. Last, but not least it is very important to offer and use an economically convenient material [6-9]. This aspect in many cases limit, at large scale, the revolution and the substitution of a very well well-tried/long standing material with a new one, like lightweight alloys, even if they reveal promising properties in some given applications. This is the case of steel, strategic material in many application, and has been used for a long time, because it is considered a material with brilliant mechanical resistance with an advantageous cost. In this situations, replacement of iron based material with other one is a very stimulating action, in particular when one talks in terms of metallurgical characteristics, and the realization of this can contribute to increase the spectrum of
real applications where these alloys can be successfully employed.

The idea of improving mechanical properties of Al-based alloy can be attained by procedures, like (i) the realization of some heat treatment [10, 11], (ii) the possibility to employ higher quantities of alloying elements [12, 13] and (iii) with the implementation of more and more efficient industrial processes in order to obtain advanced metallic alloys. Usually, heat treatment is a multi-stage process, comprising heating to an established temperature and followed by rapid quenching and aging at room temperature or higher one. Even if this procedure is the most commonly used, it is energetically and environmentally adverse and it is very time-consuming. Furthermore, the new European rules concerning the gas emissions, in particular as emission of CO$_2$ regards, is very restrictive targeting other reduction by 2030 are moving the attitude of scientist and the manufacturers to find other, alternative solutions, using stepwise evolutions, able to strongly reduce the weight of the industrial modules having a helpful effect on the fuel consumption and on the emission of CO$_2$ [14], too.

Some authors, report studies about cryogenic treatment, even if there are no adequate data to enunciate that such treatment is one of the feasible way to improve the mechanical, tribological and corrosion properties of Al-based alloy. According to such investigations [15-18], cryogenic treatment determines a reduction of the number of lattice defects compared to the un-treated samples and favour the displacement of the atoms of alloying elements. In such conditions, development of secondary phases take place giving rise to make stronger the alloy. Additionally, in the same conditions it comes out that the residual stresses in the alloy is changing, and more in particular, cryogenic treatment helps the generation of a small quantity of compressive residual stresses, more convenient for the alloy performances, and remove part of the tensile residual stresses [19, 20].

Due to the fact that Al-Zn-Mg-Cu alloys are subjected to multidirectional stresses in operation and due to the highly varying operating conditions over time, they have to reveal good structure and properties stability [21-23]. The Zn, Mg, and Cu alloying of aluminium determine superior properties as a result of the presence of the basic metallic mass of hardening phases developed and considered responsible for such behaviour according to [24].

At this time, there is an increasing need to identify the optimal operating parameters for the industrially used components. To the best knowledge of the authors of the present paper there are no sufficient study which consider and investigate the EN AW 7075 Al-based alloy at low temperature, like -70°C÷-150°C, condition which is present during the exploitation of the airplanes.

In this context, the aim of the present research paper is to investigate the structural modifications of EN AW 7075 Al-based alloy, in different initial conditions, over a wide range of temperatures. To do this thermal analysis has been used, in the temperature range of -160÷+600°C, in order to be able to appreciate the performance of the alloy in a particular condition which simulate a real exploitation environment, and based on the results obtained, to recommend it for aeronautical application.

2. Experimental methods

2.1 Material selection

For the experimental research, EN AW 7075 Al-based alloy has been used with the chemical composition reported in table 1.

| Alloy type | Chemical composition [%] |
|------------|--------------------------|
|            | Zn | Mg | Cu | Cr | Ti | Mn | Fe  | Si  | Al  |
| Standard   | 5.1-6.1 | 2.1-2.9 | 1.2-2.0 | 0.18–0.28 | 0.1max | 0.1max | 0.12max | 0.15max | balance |
| Investigated | 6.0 | 2.4 | 1.5 | 0.2 | 0.05 | 0.05 | 0.1 | 0.1 | 89.6 |

The considered alloy is situated at the limit of the homogeneous phase domain of s. s. α and of the biphasic zone α + S, according to the phase diagram reported in figure 1. As a consequence, one can admit that at the homogenization temperature the structure is single-phase made only by s.s. α. When hardening, this remain the developed structure and during the aging processes (artificial or natural) the
formation of G. P. areas occurs, corresponding to the \( \theta (\text{Al}_2\text{Cu}) \), \( Z = \text{Mg}_2\text{Zn}_{11} \), \( M (\eta=\text{MgZn}_2) \), \( T (\text{Al}_2\text{Mg}_3\text{Zn}_3) \), and \( S(\text{Al}_2\text{CuMg}) \) phases and determining the hardening of the alloy. The proportion of the phases \( \theta (\text{Al}_2\text{Cu}) \), \( Z = \text{Mg}_2\text{Zn}_{11} \) in the structure of the 7075 alloy is negligible [25].

![Quaternary phase diagram of the Al-Zn-Cu-Mg system at 733 K (460°C), for 6% of Zn [25]](image)

**Figure 1.** Quaternary phase diagram of the Al-Zn-Cu-Mg system at 733 K (460°C), for 6% of Zn [25] showing the effect of the Mg and Cu change.

Due to the fact that the T- and S- phases show low melting points, the heating range for heat treatments and hot works is limited; the S-phase content depends on the chemical composition of the alloy and on the temperature.

Some studies [26-28] indicates that the fraction of these phases in the alloy structure varies significantly depending on the composition and the ratio of the alloying elements (Zn / Mg, (Cu + Mg)). We consider that in this case, the \( \eta \) phase has a dominant role in the hardening of the alloy.

The available material, as supplied, was used to make sets of samples, in particular hardness test samples, for the resilience test (EN 10045-1: 1990) and for the tensile test (SR. EN. 10002-1) with round cross-section.

### 2.2 Sample conditioning

The samples prepared, as described above, have been subjected to the final heat treatment of quenching, natural and artificial ageing. For quenching, after holding the samples at 470 °C for one hour, they have been cooled in water. The artificial ageing has been performed by holding the samples for 2 hours at 120 °C, followed by cooling in air, while for the natural ageing the samples have been held for 7 days at 20 °C. Investigations have been performed in order to study the effects of negative temperatures on the structure and properties of the alloys: some of the heat-treated samples have been subjected to cooling cycles at -70 °C with one hour holding, followed by reheating to room temperature. Between two successive cooling, the samples have been maintained at room temperature for 30 minutes. The same parameters have been used for performing up to three cooling. Finally, the resilience has been measured, on standard parallelepiped samples (10x10x55 mm) without notch. Impact test has been performed by a Charpy impact pendulum devices of 50 J at room temperature. Five samples of each heat treatment have been tested and the average value and standard deviation have been calculated. Brinell hardness measurements have been carried out on the polished samples. A force of 10 N has been applied for 15 s for each measurement and a minimum of 5 indentations have been performed on each samples. Samples made of semi-continuous casted and rolled alloy to a thickness of 45 mm have been used to perform the experiments.

The samples have been heated in the Nabertherm furnace and have been cooled to negative temperatures in an oven-type device with a controlled atmosphere.

Thermal analysis has been carried out by dilatometric analysis (LINSEIS dilatometer, L75/230) and the measurements have been performed in a temperature range of 25-1400 °C using cylindrical
specimens, with 6 mm diameter and lengths between 5 and 10 mm, while differential scanning calorimetry (DSC, Netzsch GmbH, 200 F3 Maia type) has been performed with a heating/cooling rate of 10 °C/min., while. The specimens have been heated and cooled at a rate of 10 °C/min. The analysis of the effect of cooling below zero degrees Celsius on the phase transformations of the EN AW 7075 Al-based alloy has been performed on some heat treated samples. Table 2 reports the details of the treatment.

| Samples  | Thermal treatment applied | Number of cooling to -70°C |
|----------|--------------------------|--------------------------|
| Sample 1 | Annealed                 | -                        |
| Sample 2 | Natural aging            | -                        |
| Sample 3 | Artificial aging         | -                        |
| Sample 4 | Artificial aging         | 1                        |
| Sample 5 | Artificial aging         | 3                        |

3. Results and discussion

3.1 Dilatometric analysis

Detection of phase transformations in the field of positive temperatures has been carried out by dilatometric analysis. The results of the such investigations have been reported in figure 2 for the samples 2-5. For comparison, figure 3 shows the variation of elongation and physical expansion coefficient for the annealed alloy (sample 1) depending on the temperature.

Figure 2(a) reveals that there are differences between the samples as regards the variation of the heating expansion coefficient. This is a direct evidence on the differences between the structures of the sample and the way in which these structures evolve during heating. It should be noted that when heated, the highest structural stability is found in sample 2.

The cooling performed at negative temperatures (-70°C) do not have a significant influence on the structural changes that occur during heating.

Considering the diagram in figure 4, the first maximum on the variation curve of the expansion coefficient (figure 2(a)), from the temperature of about 190 °C, corresponds to the re-dissolution of the η' type precipitates, a phenomenon that occurs with a decrease of the volume of the alloy revealed by the decrease of the value of the expansion coefficient.

![Figure 2](image-url)

**Figure 2.** Expansion curve and variation of the physical expansion coefficient as a function of temperature at heating (a) and at cooling (b).
Figure 3. Results of the dilatometry analysis for the annealed samples.

Figure 4. Scheme for the solvus temperatures related to the different precipitates (separations).

Around the temperature of 240°C (the minimum of the curves in figure 2(a)), the process of separating of the η phase at the limits of the solid solution crystals α begins, which determines the amplification of the expansion coefficient value. In the temperature range 340°C÷350°C the increase of the expansion coefficient value becomes much more moderate, it even decreases in the case of samples 3 and 4. This step corresponds to the re-dissolution of the η phase in the α solid solution.

These relevant heating differences disappear during cooling (figure 2(b)) after homogenization, determined by heating temperatures during the DIL analysis, has taken place, when the samples have the same chemical composition.

By presenting the contraction curves and the physical contraction coefficient, in figure 2(b), is reported that in all samples, after the development of the same structure, by heating, in all samples identical structural transformations occur in the cooling phase during the dilatometric analysis. This is confirmed by the overlap of both the contraction curves and the curves corresponding to the physical contraction coefficients.

By performing DSC analyses, the aim was to explain the phase transformations in the temperature range -150÷ 590 °C. Figure 5 reports the temperature-time diagram for DSC analyses.

The thermal analysis program was identical for all samples (figure 5: cooling from room temperature (RT) to -5 °C; holding at -5 °C for 5 minutes; cooling to -150 °C; heating to 590 °C; cooling to room temperature. Both heating and cooling have been performed at a rate of 10
All measurements have been carried out in N2 protective atmosphere with a flow of 250 ml/min. The device was calibrated prior to performing the determinations. The data has been evaluated by NETZSCH Proteus - Thermal Analysis software.

The thermal regime shown in figure 5 i.e. cooling to -150 °C and subsequent heating up to 590 °C, can highlight the evolution/phase separations in/from the solid solution α, as well as their disappearance at the temperatures at which the formation of the solid solution rich in alloying elements takes place, which corresponds to the equilibrium condition. The 5 minute holding threshold at - 5 °C has been realized due to the need of eliminating any deviations due to the inertia of the device in the planned thermal regime (established during the experiment). Figure 5 reports the results obtained during these investigations, for sample 3.

The analysis of the curves reveals that in all the cases, when cooling to negative temperatures between -9 and -18 °C occurs, the presence of an exothermic maximum is observed, figure 6, which goes with a phase precipitation process within the structure (for the sample 3 it is possible to observe the exothermic peak at (-15.2°C). The phenomenon is due to the decrease in solubility of the elements within the chemical composition of the alloy in aluminium solid solution α. The elements participating most actively in this process are those that have a significant decrease in solubility with the temperature in ssα (e.g. Mg). Even if they are not of high intensity, these processes have an influence on the properties of the alloys, as reported in table 3.
Figure 7. DSC curves showing the behaviour of the samples in different conditions.
In the range of the natural aging temperature, the intensity of these precipitations is very low, considering the values of the energies corresponding to the structural transformations. At the same time, the influence of cooling to negative temperatures is observed in the sense that these transformations at higher temperatures occur and with lower intensities, which means that the treatment applied by cooling the samples to -70 are contributed to the stabilization of the structure.

In the range of temperatures corresponding to artificial aging, the intensity of structural transformations is much higher, especially in the case of samples 3 and 4, as reveals figure 7b. The values of the transformation energies indicated by the DSC curves, for the two samples, 6.492 J/g and 5.976 J/g are in accordance with those indicated in [26].

Also in this field the higher value of the transformation energy for sample 3 (artificial aging), compared to the naturally aged sample (2), proves that the structure obtained by natural aging contains in a superior proportion the phase η', hardeners, which determines improved mechanical properties (table 3).

At the same time, the domains of the transformation temperatures indicated by the DSC curves are found also on the dilatometric curves shown in figure 2(a).

In the range of homogenization temperatures (470-510°C), the DSC curves reported in figure 7(c) do not evidence significant structural transformations.

The range in which the precipitation processes continue when heating the alloy to positive temperatures and the diffusion becomes more permissive. It is possible to observe the localisation of the precipitations in two temperature zones: a zone close to the room temperature specific to the temperatures of natural ageing (figure 7(a)) and another area at higher values, specific to the temperatures of artificial ageing, as reported in figure 7(b). At the temperatures in the first zone, the precipitation is lower for the artificially aged alloy, while they are lower for the naturally aged alloy at temperatures in the second zone, phenomenon confirmed also by the results of the dilatometric analysis (figure 2(a)).

3.2 Mechanical analysis

In addition to the DIL and DSC analyses, the Brinell hardness, resilience and tensile strength at breaking have been measured. The results of the mechanical properties measured on samples under different conditions, reporting the average of three parallel determinations, have been collected in table 3.

| Sample | Heat treatment       | Number of processes of cooling to -70°C | Hardness [HB] | Resilience KCU [J/m²] | Breaking strength [N/mm²] |
|--------|----------------------|----------------------------------------|--------------|-----------------------|--------------------------|
| 2      | Natural aging        | -                                      | 130± 2       | 90± 5                 | 414± 20                  |
| 3      | Artificial aging     | -                                      | 96± 2        | 71± 5                 | 409± 20                  |
| 4      | Artificial aging 1   | 1                                      | 99± 2        | 91 ± 5                | 411± 20                  |
| 5      | Artificial aging 3   | 3                                      | 128± 3       | 86 ± 5                | 406± 20                  |
| 6      | Natural aging 1      | 1                                      | 133          | 68 ± 5                | 413 ± 20                 |
| 7      | Natural aging 3      | 3                                      | 139          | 65.8 ± 5              | 410 ± 20                 |

The values of the considered properties obtained by natural ageing are higher with respect to those obtained by artificial ageing. This fact is due to the particularity of the formation of the structural phases that control these properties in such situations. In natural ageing, these phases have developed at low temperatures (room temperature) and the diffusion of the elements arises with more difficulty, so that a higher germination rate/growth rate (vg/vc) is achieved. Under these conditions, the phase
distribution in the structure is finer and more homogeneous, with direct consequences on the increase of mechanical properties.

As a result of cooling, the materials at negative temperatures after ageing (in one or more cycles), show variations as mechanical properties concern. These deviations can be attributed to some transformations in the structure, consisting in the persistence of the transformation in the state of the hardening phases: the α solid solution of the alloy becomes unstable at certain negative temperatures at which the evolution of the precipitate occurs, influencing the properties of the material. The significant decrease of the resilience values suggests the fact that the structural changes determined by the application of cooling to negative temperatures, the proportion of the hardening phases changes, fact indicated by the DSC curve reported in figure 7, by increasing the existing ones and not by germination. This fact determines the brittleness of the alloy, a phenomenon that appears during the exploitation at negative temperatures of the subassemblies that include elements of this composition.

4. Conclusions
In this paper, structural analysis of the EN AW 7075 Al-based alloy, in different condition, was carried out to determine if such alloys can be proposed as a good candidate for applications where has to survive also at low temperature. Based on the results obtained by dilatometric analysis, the cooling performed to negative temperatures (-70°C) do not have a significant effect on the structural modifications that take place during heating. DSC analyses results, performed with the aim to clarify the phase transformations in the temperature range -150÷ 590 °C, support the results coming from dilatometric measurements. At the same time, the DIL and DSC analyses allowed the formulation of some assumptions regarding the mechanism of increasing the proportion of the hardening phase, ie by germination/deposition. As a result of cooling, the materials at negative temperatures after ageing (in one or more cycles), demonstrate some modifications as its mechanical performance regards, attributable to some transformations within its structure, and the persistence of the transformation in the state of the hardening phases. However, reduction of the resilience values was observed and for this reason, some preventive measure has to be considered during the exploitation of such alloy at negative temperatures, which is the case of aeronautical application.

5. References
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