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Ing. Costan Ecaterina (căs. Ware)

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Early stage precipitation mechanisms in Al-Mg-Si alloys with improved mechanical properties for automotive industry applications

Conducător științific
Prof.dr.fiz. Traian Petrișor

Conducător științific
Acad. Dorel Banabic

Comisia de evaluare a tezei de doctorat:

PREŞEDINTE:	- Prof.dr.ing**. Liviu Nistor** - Universitatea Tehnică din Cluj-Napoca;
Conducător ştiinţific:	- Prof.dr.fiz. **Traian Petrișor** - Universitatea Tehnică din Cluj-Napoca;
Conducător ştiinţific:	- Acad. **Dorel Banabic** - Universitatea Tehnică din Cluj-Napoca;
Referenţi:	- Prof.dr.ing**. Doina Răducanu** - Universitatea Politehnica din București;
	- Prof.dr.ing. **Daniel Munteanu** - Universitatea "Transilvania" din Brașov;
	- Prof.dr.ing. **Ionel Chicinaș** - Universitatea Tehnică din Cluj-Napoca.

str. Memorandumului nr.28, 400114 Cluj-Napoca, România
tel. +40-264-401200, fax +40-264-592055, secretariat tel. +40+264-202209, fax +40-264-202280
http://www.utcluj.ro/

CONTENT

Abbreviations

ABS	Anti-lock braking system
ADLD	Advance Delay-Line Detector
AFM	Atom Force Microscopy
APFIM	Atom Probe Field Ion Microscopy
ARAMIS	Digital Image Correlation Software
BF	Bright Field
BH	Bake Hardening Steel
BS	Boron Steel
CBED	Convergent Beam Electron |Diffraction
CCD	Charged-Coupled Device
CERTETA	Research Centre in Sheet Metal Forming
CMn	Manganese Alloyed Steel
DF	Dark Field
DP	Dual-Phase Steel
EDS	Energy Dispersive X-Ray Spectroscopy
EW	Exit Wave function
DW	Debye Waller
FEG	Field Emission Gun
FIM	Field Ion Microscopy
GP	Guiner Preston
HOLZ	High Order Laue-Zone
HRTEM	High Resolution Transmission Electron Microscope

HSLA	High-Strength Low-Alloy Steel
HV	Vickers Hardness
IF	Interstitial Free Steel
ISO	International Standard Organisation
MART	Martensitic Steel
NA	Natural Ageing
nS	neutron Scattering
PALS	Positron Annihilation Lifetime Spectroscopy
PAS	Positron Annihilation Spectroscopy
PAS-LT	Positron Annihilation Spectroscopy Life Time
Q	Particle/Phase developed in Al-Mg-Si-Cu Alloys
QBHR	Quick Bake Hardening Response
RT	Room Temperature
SADP	Selected Aria Diffraction Pattern
SAED	Selected Aria Electron Diffraction
SHT	Solution Heat Treatment
SLC	Super Light Car
SSSS	Supersaturated Solid Solution
STM	Scanning Tunnelling Microscopy
T4	Solution Heat Treated and Naturally Aged Aluminium Alloy
TEM	Transmission Electron Microscopy
TF	Through Focus
TF-EWR	Through Focus Exit Wave Function Reconstruction
TPVF	Total Precipitate Volume Fraction
TRIP	Transformation Induced Plasticity Steel
TWIP	Twinning-Induced Plasticity Steel
VER	Volume Expansion Retio

Overview

Transmission Electron Microscope was the most used tool in this work. A Transmission Electron Microscope (TEM) is a complex assembly including: electromagnetic lenses, several apertures, a sample holder and an image recording/viewing system. The magnetic lenses can be grouped into the following two general types:

1. Those of illumination system between the electron gun and the sample,
2. Those of the imaging system after the sample.

In TEM one can switch between image mode and diffraction mode by changing the strength of the intermediate lens. To observe the diffraction pattern, the intermediate lens is adjusted to focus onto the back focal plane of the objective lens; i.e. the back focal plane of the objective lens acts as the object plane for the intermediate lens. In imaging mode, the intermediate lens is adjusted so that its object plane is the image plane of the objective lens.

The primary imaging mode takes advantage of mass contrast, or diffraction contrast, to image the internal microstructure of materials. This is commonly used to image grain and defect structures (i.e. dislocations, voids, staking faults and twins, etc.) within materials. Precipitates or inclusions are also easily observed using this technique.

It is possible to view and record the electron diffraction pattern from a selected area of the specimen as small as ~ 1 μm by placing an aperture in the image plane and then projecting the diffraction pattern of the image onto the recording plane. Nanodiffraction is a special form of SAED in which the emphasis is on obtaining diffraction patterns from regions of the specimen of about 10 nm or less in diameter. To record diffraction patterns with relatively sharp spots, a Field Emission Gun (FEG) is needed. Contrastingly, with SADP the diffraction area is selected by focusing the electron beam. The primary purpose of electron diffraction techniques is to identify the unit cell, or the crystal structure, of the materials under investigation, or to orient the crystal in a given zone.

High-resolution transmission electron microscope (HRTEM) is a powerful imaging technique for obtaining atomic resolution structural information. It allows experimental exploration of thin specimens on a nanometer scale at sub-Angstrom resolution. Recent technological improvements allow a resolution of approximately 0.1 nm so that it becomes possible to “see” the individual atomic columns (rows of atoms along the viewing direction, which may be separated at by about 0.2 to 1 nm in the viewing direction), in a relatively large number of directions.

Using CCD cameras, this information can be sampled and stored for quantitative comparison between simulated versus experimental results. Such a comparison is necessary because, except under quite strict conditions, the images formed are not directly interpretable. This is due to the combination of the incoherence effect, and from aberrations in the optical system, and additionally due to the modification of the incident beam upon transmission through the sample. Typically, a wave function reconstruction performed using a high-resolution transmission electron microscope is affected by varying defocus to measure a series of images, and utilising this information to reconstruct the wave function at the exit surface of the specimen.

In Chapter II, the history of precipitation hardening is reviewed briefly. Next, the results of previous studies of the natural ageing of Al-Mg-Si alloys are presented. This begins with an overview on the aging sequence of 6xxx series alloys. The meaning of 6xxx is the as follows. 6 indicates the principal alloying element, which has been added to the aluminium alloy and is often used to describe the aluminium alloy series, in this case the 6000 series. The second single digit (xXxx), if different from 0, indicates a modification of a specific alloy, and the third and fourth digits (xxXX) are arbitrary numbers given to identify a specific alloy in the series. This summary is followed by a discussion of the effect of low and intermediate ageing temperatures on these alloys’ properties. Finally, the paint bake cycle and the parameters affecting it are discussed.

In Chapter III, is presented the current study of materials used in car body industry. Due to evolutions in car industries, the quantity of ferrous materials has diminished. Significantly, cast aluminum has iron based alloys for engine construction. Plastic materials have a significant role in reducing steel sheets useage, besides the use of aluminum use for wheel rims and suspension. Another important factor constraining car manufacturers to use light materials, for various components, is the economic and environmental requirements for reducing fuel consumption. Aluminium alloys are used widely in car body structure, chassis and suspension parts. Aluminium alloys are especially utilised for sport and luxury cars. Besides various Mercedes models, the Audi A2 uses the alloy for small cars and high car production. The most commonly-used aluminium alloys in the car industry is the 6xxx series. The main alloying elements of these alloys are magnesium and silicon (approximately 1% each). Aluminium alloys have attracted considerable interest from the automotive industry in the last few years, as manufacturers seek to design lightweight vehicles having both improved fuel efficiency and reduced CO_2 emissions. Heat-treatable Al-Mg-Si alloys (6xxx series) are, in particular, increasingly used in automotive applications for this reason. Heat-treatable alloys have the advantage of combining both good formability after solution-treatment and quenching and high strength after age hardening, during the automotive paint bake process at approximately 185ºC. The paint bake process increases the strength of Al-Mg-Si alloys due to precipitation hardening, and, at the same time, enables the curing of the paint.

Chapter IV is presenting early-stage precipitates in the Al-Mg-Si based 6xxx alloys include solute clusters, GP-zones (including pre-β” phase), the β” phase as well as the so called Q particles, if small amount of Cu is added in the alloys. Using high resolution transmission electron microscopy and quantitative electron diffraction, these precipitates are studied in details. The β” phase has a monoclinic structure with the composition Mg_5Si_6. The structure of the pre-β” phase is quite like that of the β” phase but the atom positions are more close to that the Al lattice. It is pinpointed out that Al poorly-develops many of the structures of the precipitates, due to the presence of defects and substitutions of Mg and Si.

In Chapter V atomic resolution electron microscopy reveals that pillarlike silicon double columns exist in the hardening nanoprecipitates of Al-Mg-Si alloys, which vary in structure and composition. Upon annealing, the Si_2 pillars provide the skeleton of the nanoparticles to evolve in composition, structure and morphology. We show that they begin as tiny nuclei with a composition close to $Mg_2Si_2Al_7$ and a minimal mismatch with the aluminium matrix. They subsequently undergo an onedimensional growth in association with compositional change, becoming elongated particles. During the evolution towards the final Mg_5Si_6 particles, the compositional change is accompanied by a characteristic structural change. Our study explains the nanoscopic reason that the alloys make excellent automotive materials.

In Chapter VI is presented the mechanical characterisation of the AA6016 alloy. This aluminium alloy is used in cars manufacturing. It belongs to 6xxx alloys series of aluminium alloys, being used as deformed product. This alloy has medium mechanical characteristics, the reinforcing phase being the metastable precipitate of Mg_5Si_6 in aluminium matrix. AA6016 alloy presents very good corrosion proof properties, delivered in T4 hardening condition (solution hardening followed by natural ageing) for a better resistance to parts painting of these types of aluminium. The tensile testing aims to mechanically determine the most important parameters describing the mechanical resistance of the metallic materials. These parameters are used for cold compressing when choosing half-finished parts. Employing uniaxial traction test, the tensile – deformation characteristic curve shall be traced for some samples collected from a thin sheet. In this work hardness test and tensile test was used as mechanical testing. The hardness test is very simple and easy. Nevertheless, it can give a very good and precise indication of the precipitation process. The big advantage of the hardness test is the possibility of using in-situ samples – doing the measurements while they are being aged. Rockwell hardness measurements were performed on 8 samples according to ASTM E18-07 Standard. A standard Rockwell 1/8" ball indentor was used with a load of 60 kg. For each indentation point, at least 6 measurements were taken and the average was calculated. All these tests, were performed at room temperature and for the shortest possible time to avoid the natural ageing of the samples. From a general point of view, positron annihilation spectroscopy is a powerful tool for microstructure investigation, a spectroscopic technique for study of vacancy type defects as well as very low concentration of defects and it is a suitable technique for defects study in the near surface region. Positron-Lifetime measurements consist of infecting positrons into the sample and measuring their lifetime spectrum. The advantage of this isotope is that its most frequent decay channel is the emission of a photon, 1.274 MeV, coinciding with the positron. This property is a very useful one because the 1.274 MeV photon gives the signal that indicates the birth of the positron. The signal of annihilation is either one of the two annihilation photons, about 0.511 MeV, coming from the conversion in electromagnetic energy of the mass of the annihilated particles. In other words, the positrons are anti-particles of electrons and their lifetime depend on the density of the electrons. Therefore, any fact that can change the electron density can change the positron survival probability around it. Positron lifetime could be changed by very simple defects in the metal matrix like mono-vacancies, or dislocations, grain boundaries, voids. Hardness measurements were taken after solution heat treatment performed at 525°C and 560°C, provides a 50% difference in the total concentration of vacancies. Quenching the samples from 525°C and 560°C respectively, should be executed fast enough to avoid a significant vacancies loss during the process. The most controllable way of quenching is using water at room temperature. There are many techniques for precipitation process investigation but not all the techniques are applicable for the clustering study (very early stage precipitation). Extremely small size of these clusters, aligned perfectly with the aluminium matrix (perfectly coherent with the matrix), makes their observation very difficult, almost impossible. These clusters are parts of the matrix which have a higher concentration of solute atoms than the rest of it. Therefore, one focussed in other techniques which can give an indirect evidence of these clusters existence. Electrical resistivity is a classical technique for analysing early stage precipitation. The resistivity signal provides information not only about the actual clustering but also about vacancies and solute atoms. Therefore, to interpret the results of this measurement, other types of analysis are required like positron annihilation lifetime spectroscopy (PALS). This analysis will provide information about vacancies during the clustering process. PALS is an old technique used in physics. Nevertheless, the application of PALS in the study of clustering is quite new. The hardness testing was applied on each sample. That can demonstrate the definite effect of clustering at the macroscopic level. Hardness testing is a very simple technique and one were considering to apply it in this work.