Deliverable Report

Deliverable Title:

Description of criteria and tools used for exploring alternative alloying system,

and for performing process vs microstructure optimisation

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Summary

After the identification of the base-systems for the development of SALEMA alloys, i.e.:
- AlSi10MnMg, AlMg and Al4MgFe systems for HPDC Demonstrators,
- 5000 and 6000 series for Wrought (Extrusion, Stamping) Demonstrators,

criteria and tools must be applied for individuating the specific alloys to be used in experimental campaigns.

The strategy and the criteria to be developed and implemented to minimise CRM content must be focussed, obviously, on Mg and Si amounts, whose reduction needs to be compensated by elements and/or treatments offering good technological and mechanical performance. This means considering the options offered both by

- elements such as Mn, Cu, Zn (solid solution strengthening) and Ti (grain refinement) for both HPDC and wrought alloys,
- optimisation of work hardening and heat treatment conditions for wrought alloys,

and thus adopting proper models to quantitatively describe the effect of these elements and conditions on mechanical behaviour of the alloys.

Furthermore, alloys need to be processed, according to the specific components to be manufactured, by HPDC, extrusion or stamping. In all these cases, peculiarities of foundry, extrusion and stamping processes must be considered by specific models and tools suitable for evaluating castability performance for HPDC alloys (which means a combination of fluidity, solidification shrinkage, slag/dross formation tendency, die soldering tendency, hot tearing tendency) and attitude to hot working (for extrusion and stamping alloys).

This Deliverable reviews the theoretical models more suitable for describing the above-mentioned key-characteristics required for alloys. Based on such models, state-of-the-art or properly developed tools supporting SALEMA alloys design and selection are presented and discussed in view of their implementation in the frame of Deliverable D2.3.

Disclaimer

Abbreviations

Abbreviation / Acronyms	Description
A	Elongation at break
ARL	Abundance Risk Level
CI	Criticality Index
CI_{CRM}	Criticality Index for Critical Raw Material
CRM	Critical Raw Materials
DSI	Die Soldering Index
EC	European Commission
ECR	Environmental Country Risk
EI	Economic Importance
EIn	Extraction Index
HPDC	High Pressure Die Casting
NEI	Normalized Economic Importance
NSR	Normalized Supply Risk
PC	Project Consortium
PMT	Project Management Team
PSB	Project Steering Board
RDI	Recycling Drawback Index
RM	Raw Material
SF	Sludge Factor
SGR	Sourcing and Geopolitical Risk
SR	Supply Risk
TA	Temperature of ageing
tA	time of ageing
TFR	Terminal Freezing Range
UTS or Rm	Ultimate Tensile Strength
YS or ReH	Yield Strength
WP	Work Package

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1. Criteria to be followed for exploring alternative alloying systems

1.1. Outcome from Task 2.2. and approach of Deliverable D2.2

Deliverable D2.1 individuated the specifications required by the low CRM aluminium alloys to be developed in the frame of SALEMA activities, referred to the following base-systems:

- AlSi10MnMg, AlMg and Al4MgFe systems for HPDC Demonstrators
- 5000 and 6000 series for Wrought (Extrusion, Stamping) Demonstrators.

The strategy and the criteria to be developed and implemented to minimise CRM content must be focussed, obviously, on the main alloying elements amounts, Mg and Si, whose reduction needs to be compensated by elements and/or treatments offering good technological and mechanical performance. This means considering the options offered both by

- elements such as Mn, Cu, Zn (solid solution strengthening) and Ti (microalloying for grain refinement purpose only) for both HPDC and wrought alloys
- optimisation of work hardening and heat treatment conditions for wrought alloys

Furthermore, peculiarities of foundry, extrusion and stamping processes must be considered by specific models suitable for evaluating castability performance (for HPDC alloys) and attitude to hot working (for extrusion and stamping alloys).

The approach adopted in this Deliverable is that of considering, for each group of alloys targeted (for HPDC, for extrusion and for rolling & stamping) the theoretical models more suitable for describing the key-characteristics required. Based on such models, state-of-the-art or properly developed tools have to be adopted for the evaluation of the characteristics mentioned above. The overall scenario investigated in this Deliverable is summarised in Table 1, showing, with reference to SALEMA context, which kind of models are applied for each group of alloys.

		Alloy Group		
Conceptual area	**Characteristic of phenomenon to be modelled**	**For HPDC**	**For extrusion**	**For rolling & stamping**
CRM content	Criticality Index	√	√	√
Castability	Fluidity (as the inverse of viscosity)	√		
	Solidification shrinkage	√		
	Slag/dross formation tendency	√		
	Die soldering tendency	√		
	Hot tearing tendency	√		
Hot working attitude, extrudability	Solid solution element at processing temperature		√	√
Mechanical compensation of Si and Mg decrease in alloys	Alternative elements for solid solution strengthening	√	√	√
	Grain refinement	√		√
	Improving of heat treatment	√	√	√
	Improving work hardening			√

Table 1 – Kind of models adopted in SALEMA context with respect to the specific group of alloys under investigation

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The above listed models can be classified in three categories:

- **models properly developed by the Authors of this Deliverable,**
- **models already implemented in the commercial software Thermo-Calc (see Annex 1),**
- **models developed by elaborating some of Thermo-Calc results.**

Details of these categories are collected in Table 2.

Conceptual area	Characteristic of phenomenon to be modelled	Category of model
CRM content	Criticality Index	Properly developed
Castability	Fluidity (as the inverse of viscosity)	Thermo-Calc Software
	Solidification shrinkage	△ + elaboration
	Slag/dross formation tendency	△ + elaboration
	Die soldering tendency	△ + elaboration
	Hot tearing tendency	△ + elaboration
Hot working attitude, extrudability	Solid solution element at processing temperature	Properly developed
Mechanical compensation of Si and Mg decrease in alloys	Alternative elements for solid solution strengthening	△ + elaboration
	Grain refinement	Properly developed
	Improving of heat treatment	Properly developed
	Improving work hardening	Properly developed

Table 2 – Categories of the models adopted in this Deliverable

Thus, the selection of alloys systems to be produced and investigated in the further stages of SALEMA Project, is based on the following strategy:

- **evaluation of the above listed characteristics, depending on the process addressed, e.g. castability for HPDC alloys (i.e. fluidity, considered as the inverse of viscosity, solidification shrinkage, slag/dross formation tendency, die soldering tendency), by developing and/or individuating models and tools to calculate these characteristics from alloys composition,**
- **estimation of mechanical performance of alloys achievable by replacing of Si and Mg with other elements or by optimising heat treatment or work hardening parameters,**
- **associating each composition to the corresponding Criticality Index, properly calculated for each alloy,**
- **applying these models and tools to a wide set of compositions (subject of Deliverable D2.3),**
- **selecting the specific systems offering the (theoretical) best compromise among processing properties, expected performance and low criticality characteristics (subject of Deliverable D2.3),**
- **Performing experimental campaigns to verify “in field” the optimal solutions, to be finally implemented in industrial production (subject of Deliverable D2.4).**

2. Criteria and tools for evaluating Criticality Index

2.1. Criticality of Raw Materials

The world is approaching to a new era in which sustainability is one of the key factors. Sustainability is inevitably linked, among the others, to lightweight design which in turn depends on multi-materials products development. Today cars are an easy example in which advanced high strength steel, composites, polymeric materials as well as light alloys are extensively used together to maximize the performances, reduce weights and therefore the polluting gases emission. Weight reduction is an imperative goal also because of the growing importance given by Europe to new strategic sectors or technologies such as e-mobility, drones, robotics, 3D printing, defence and aerospace. Focusing on light alloys, such as magnesium, aluminium, beryllium or titanium alloys, that cannot be substituted by composites or polymers when the working temperature exceeds 200-300 °C, it is noted that they suffer from a high criticality issue according to European Community (EC) [1]. A Raw Material is considered critical according to different criteria or indicators that quantify the economic importance (EI), the supply risk (SR), the recyclability input rate, the substitutability issue, etc. The critical raw materials list is updated every three years and the last report dates September 2020 [1]. It is worth mentioning that the criticality assessment of raw materials is not an easy task and that there is not a recognized method to reach that goal in literature [2,3]. In a recent paper, Hofmann et al. [4] showed that material scientists seem frequently not concerned with the criticality of raw materials in their work so that they suggested to advance the implementation of the concept of materials criticality in materials research and development. In this scenario, Ferro et al. [5-8], in the frame of Ashby's material selection method [9], developed a procedure to assess the material's index containing information about criticality. Finally, it is worth mentioning that the criticality concept is very relative since it depends on the Country where it is formulated. In fact, the supply risk, for instance, is a geopolitical factor, based on the natural resources of a country; the technology to process, and to recycle, a raw material also varies from country to country, and it affects both the SR and the EI; and last, but not least, the strategic technologies and the strategic sectors, also vary through the globe. It is noted, in fact, that, since defence, drones and robots are today considered strategic sectors for Europe, the updated CRM list contains titanium as well as bauxite, among the others, as new critical raw materials [1]. Aluminium is not a CRM yet, but, obviously, bauxite can be related to primary aluminium production used in the fabrication of high performances aluminium alloy components. Magnesium and Beryllium, as well, were present in the previous 'blacklist' and still lays in the new one.

Since the product efficiency strictly depends on CRMs, it is clear that the raw materials criticality concept must be urgently included in the lightweight design. Materials that minimize the component weight don't necessary reduce the criticality issues related to their CRMs content; thus, a multi-objective strategy taking advantage from trade-off diagrams is necessary.

2.2. Critical Raw Materials and Criticality Assessment

According to the European Commission, Raw Materials (RM) are classified basing on their supply risk (SR) and economic importance (EI) values. In particular, CRMs are those RM that are characterized by a SR ≥ 1 and an EI ≥ 2.8. Figure 1 shows the CRMs list (red points) dated 2017 and the new one, dated 2020. It is interesting to observe the increasing trend of criticality for all raw materials in 2020 compared to 2017 as well as the new added CRMs, i.e., bauxite, titanium, lithium, and strontium. Niobium, for example, increased both its SR index value and its EI index. Niobium, in fact, has a primary role in high-strength stainless steel and super-alloys for most strategic technologies (i.e. in 3D printing, drones, wind turbines and robotics).

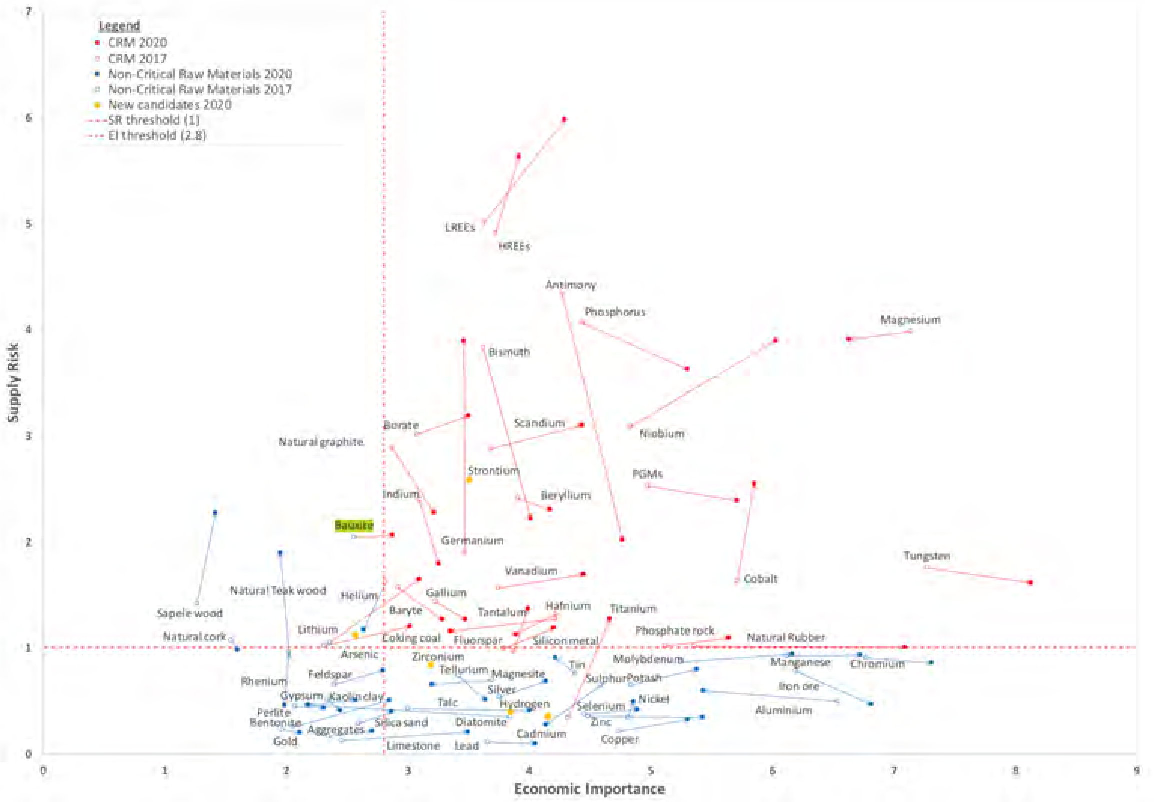


Fig. 1 – European Raw Materials classification according to EI and SR: 2017 list versus 2020 list

Moreover, Niobium is also foreseen to be used in future anode and cathode materials for electric batteries that are the most crucial strategic technology since it also serves robotics, drones and digital technologies and it is relevant for all the strategic sectors considered by the European Union. Dealing with light metals (Mg, Ti, primary Al), all of them are practically critical since even if Al doesn't take part to the blacklist directly, it is considered critical in its primary form coming from bauxite.

It is worth mentioning that the criticality issue linked to RMs it's a very complex drama that for its nature cannot be reduced to the definition two indicators only (say, SR and EI). This is the reason why other aspects of the RMs criticality need to be quantify by other indicators such as the abundance risk, the sourcing and geopolitical risk, the environmental country risk and, finally, the end-of-life recycling input rate. In order to be able to use all of them in lightweight design, it is convenient to find an aggregation procedure [10] to reduce all the criticality indicators in an overall general indicator for each critical raw material. One possibility should take the normalized value of each index to remove the units and reduce them to a common scale. Then, they may eventually be weighted to reflect the perceived seriousness of each criticality, and finally, the weighted, normalized measures should be summed or averaged to give the indicator. For the sake of simplicity, in the approach adopted by SALEMA Project, the criticality indicator for a CRM 'i' (CI_{CRMi}) is obtained by averaging the different normalized criticalities indexes as follows:

$$CI_{CRM_i} = (k_{ARL} ARL_i + k_{SGR} SGR_i + k_{ECR} ECR_i + k_{NSR} NSR_i + k_{NEI} NEI_i + k_{RDI} RDI_i)/6 \qquad (1)$$

where *k* is a non-dimensional coefficient which value is in between 0 and 1, according to the seriousness of the corresponding criticality aspect, ARL_i is the normalized value of the Abundance Risk Level of the CRM 'i', SGR_i is the normalized value of the Sourcing and Geopolitical Risk of the CRM 'i', ECR_i is the normalized value of the Environmental Country Risk of the CRM 'i', NSRi is the normalized Supply Risk of the CRM 'i', NEI_i the normalized value of the Economic Importance index of the CRM 'i' and finnaly RDI_i is the normalized value of the Recycling Drawback Index of the CRM 'i'. Detailed description of each of the aboved mentioned normalized criticality indicators can be found in references[11], while the 2020 updated list of their values is collected in Table 3. It can be observed how the highest CI values are reached by rare earth elements and palladium metals group. However, the most 'critical' materials, among those used in Aluminium alloys, are those marked with yellow.

CRM	ARL	SGR	ECR	NSR	NEI	RDI	**CI**
Sb	6.22	6.47	6.44	3.22	5.92	3.33	5.27
Ba	3.03	2.15	2.16	2.03	4.09	9.76	3.87
Bx	0.64	1.24	1.18	1.33	3.56	10.00	2.99
Be	5.50	4.56	4.46	3.74	5.22	10.00	5.58
Bi	6.62	7.46	7.44	3.72	5.00	10.00	6.71
B	4.59	2.39	2.39	5.14	4.31	9.76	4.76
Co	4.59	5.38	4.21	4.14	7.40	4.76	5.08
Cc	-	3.73	3.72	1.98	3.78	10.00	-
Fl	3.08	5.17	5.13	1.94	4.15	9.76	4.87
Ga	4.58	7.47	7.44	2.07	4.33	10.00	5.98
Ge	5.68	7.47	7.45	6.32	4.33	9.52	6.80
Hf	5.09	2.64	2.00	1.76	4.84	10.00	4.39
In	7.08	3.09	3.02	2.88	3.90	10.00	4.99
Li	4.44	1.72	1.98	2.68	3.86	10.00	4.11
Mg	1.50	9.18	9.16	6.42	7.49	6.90	6.78
Gr	5.82	5.75	5.76	3.71	4.05	9.29	5.73
Nr	-	2.03	2.00	1.62	8.82	9.76	-
Nb	4.74	8.55	7.63	6.38	7.40	10.00	7.45
Phs	2.71	2.97	2.95	1.82	7.03	5.95	3.91
P	2.71	6.55	6.54	5.84	6.61	10.00	6.37
Sc	4.68	5.93	5.69	5.32	5.52	10.00	6.19
Si	0.00	5.16	5.14	1.93	5.24	10.00	4.58
Ta	5.87	2.70	2.58	2.19	4.98	10.00	4.72
Ti	2.02	0.83	0.88	2.02	5.82	5.48	2.84
V	3.84	3.42	3.34	2.72	5.56	9.52	4.73
W	5.54	7.82	7.80	2.57	10.00	0.00	5.62
Sr	3.26	2.60	1.99	4.42	4.39	10.00	4.44
Ir	10.48	7.84	8.89	5.08	5.21	6.67	7.36
Pd	9.11	3.33	2.99	1.93	8.67	3.33	4.89
Pl	9.12	4.94	5.51	2.62	7.41	4.05	5.61
Rh	8.82	6.11	6.86	3.62	9.25	3.33	6.33
Ru	9.29	8.00	9.08	5.96	5.06	7.38	7.46
Ce	4.02	8.58	8.56	9.69	4.43	9.76	7.51
Nd	4.39	10.00	10.00	9.49	5.96	9.76	8.27
La	4.33	10.00	10.00	9.08	1.91	9.76	7.51
Pr	4.97	8.58	8.56	8.63	5.38	7.62	7.29
Sm	5.15	8.58	8.56	10.00	9.09	9.76	8.52
Eu	5.82	8.58	8.56	4.95	4.06	0.95	5.49
Tb	5.98	8.58	8.56	7.50	5.14	8.57	7.39
Gd	5.22	8.58	8.56	9.20	5.83	9.76	7.86
Er	5.46	8.58	8.56	9.60	3.87	9.76	7.64
Dy	5.23	8.58	8.56	9.59	8.96	10.00	8.49
Y	4.50	8.58	8.56	6.83	4.29	2.62	5.90
Ho	5.86	8.58	8.56	10.00	4.18	9.76	7.82
Tm	6.35	8.58	8.56	10.00	4.18	9.76	7.90
Lu	6.33	8.58	8.56	10.00	4.18	9.76	7.90
Yb	5.53	8.58	8.56	10.00	4.18	9.76	7.77

Table 3 – Criticality indicators value (grey: Palladium Group Metals (PGMs); blue: Light Rare Earth Elements, LREEs; green: Heavy Rare Earth Elements, HREEs; yellow: materials typically used for Aluminium alloys, where Bx (bauxite) should be considered equivalent to primary Al.

Since in a general alloy chemical composition different elements are present including CRMs, it is reasonable to assess the alloy criticaliy issue by using the following defined index:

$$CI_A = \sum_{i=1}^{n} CI_{CRMi} \cdot P_{CRMi} \tag{2}$$

where n is the number of CRMs in the alloy chemical composition and P_{CRMi} is the weight amount of CRM 'i' in the alloy. It is observed that the alloy criticality index (CI_A) represents an overall criticality value per unit of mass of the alloy. In a CRMs perspective, the objective to be minimized will be the criticality of the designed component. This objective is formulated by multiplying the mass of the component (m) by the alloy criticality index (Eq. 2) [8]:

$$m^* = m \cdot CI_A \tag{3}$$

Since CI_A represents an overall criticality value per unit of mass of the alloy, m* quantifies the criticality of the whole component in a CRMs perspective.

2.3. Evaluation of Criticality Index for SALEMA alloys

On the basis of the above-described approach, it has been possible to develop a specific tool for evaluating and quantifying Criticality Index for alloys. Such tool is constituted by excel database, aimed at assessing the criticality index (CI_A) for each alloy.
On one side, the database contains information of alloy designation, condition, and chemical composition, with reference to the most common and already standardised light alloys. Elements that are critical, basing on European Commission resolution, are coloured in orange and the corresponding value of the overall criticality index (CI_{CRM}) is indicated, as well (Figure 2), on the basis of equations (1). (2) and (3). Such value is linked to that of the Critical Raw Materials list (Table 3) for an easy future update of criticalities values provided by the European Commission (EC).

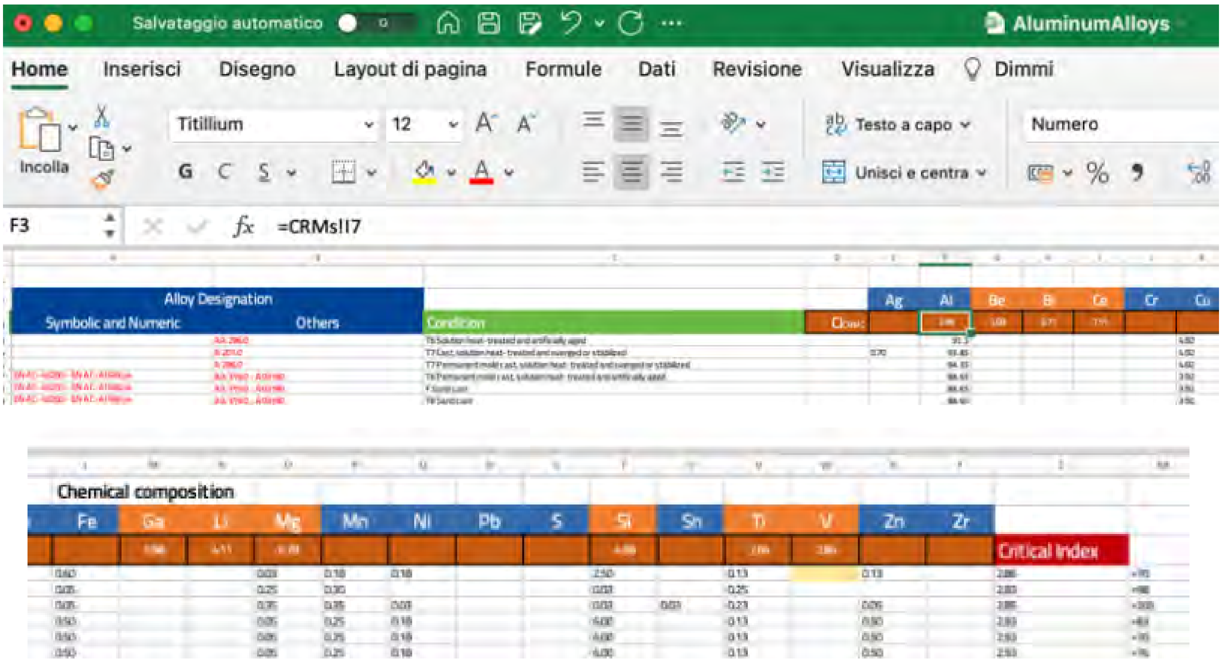
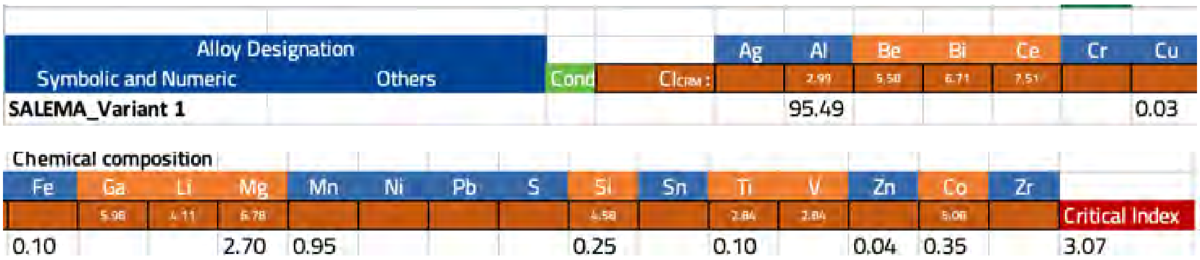


Fig. 2 – Aluminum alloys database for the alloy criticality index calculation

On the other side, the **CI_A assessment** for a specific alloy can be achieved simply by inserting its composition, in the above-described excel file.

Figure 3 shows, as an example, the evaluation of CI_A for the Variant 1 of the Al-Mg system.



Alloy Designation				Ag	Al	Be	Bi	Ce	Cr	Cu
Symbolic and Numeric	Others	Cond	CI_{CRM} :		2.99	5.50	6.71	7.51		
SALEMA_Variant 1					95.49					0.03

Chemical composition

Fe	Ga	Li	Mg	Mn	Ni	Pb	S	Si	Sn	Ti	V	Zn	Co	Zr	
	5.98	4.11	6.78					4.58		2.84	2.84		5.08		Critical Index
0.10			2.70	0.95				0.25		0.10		0.04	0.35		3.07

Fig. 3 – CI_A assessment of SALEMA VARIANT 1 (Al-Mg system)

3. Criteria & tools to evaluate castability of HPDC alloys

3.1. The concept of castability

Castability is a very general term, which implies ease of producing a casting, minimising cost, defects and lead-time. It is the result of high compatibility between product requirements and process capabilities. Generally speaking, three aspects of product design influence its castability: material selection, geometry planning and quality specification (Figure 4).

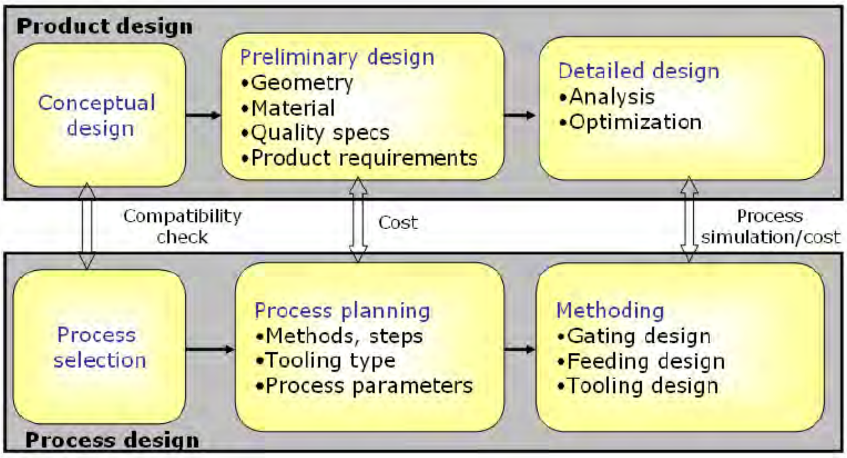


Fig. 4 – Integrated product-process design for castability [12]

This Deliverable is focussed on definition of possible alternative alloying systems, i.e. on the material-side of castability. In this sense, castability can be seen as a technological property of metals and alloys, associated to set of various conditions, parameters and characteristics, such as pouring temperature, fluidity, solidification shrinkage, slag/dross formation tendencies, etc..

Thus, the evaluation of castability of alloying systems must be defined and optimised by considering the effect that composition has on

- **Fluidity (which, in a simplified approach, can be considered as the inverse of viscosity)**
- **Solidification shrinkage,**
- **Slag/dross formation tendency,**
- **Die soldering tendency,**
- **Hot tearing tendency.**

The comprehensive evaluation of castability derives from an integrated view of such characteristics, measured in experimental tests, which may be highly time consuming.

For this reason, a good strategy is that of

- **Developing and/or individuating models to calculate these characteristics as a function of alloys composition,**
- **Applying these models to a wide set of compositions (subject of Deliverable D2.3),**
- **Associating these compositions to the corresponding Criticality Index (as described in Deliverable D2.1),**
- **Selecting the specific systems offering the (theoretical) best set of good castability & low criticality characteristics (subject of Deliverable D2.3),**
- **Performing experimental campaigns to verify “in field” the optimal solutions, to be finally implemented in industrial production (subject of Deliverable D2.4).**

3.2. Fluidity and viscosity

Fluidity is one of the alloy dependent phenomena that determine castability. Fluidity is, in casting terminology, the distance to which a metal, when cast at a given temperature, will flow in a given test mould before it is stopped by solidification. Fluidity is therefore a length, usually measured in millimetres or metres. Deliverable D2.1 already reported the description of the most used systems for testing fluidity in molten metals and alloys, which are usually time-consuming.
To achieve a good overview of fluidity performance of the wide sets of Aluminium alloys addressed by SALEMA Project, the solution adopted is that of considering viscosity (which is usually defined as the inverse of fluidity) as the reference property. Viscosity is used to describe the fluid resistance to flow, and it is the ratio of the shearing stress to the velocity gradient. Therefore, viscosity is a very important physical property of melts for the solidification simulation of the industrial cast metals and the modelling associated with fluid flow. Viscosity has been known for a long time, and its evaluation can be done based on models considering thermo-physical properties of pure metals and combining them to predict behaviour of alloys. From experimental data and theoretical analyses, an Arrhenius-type equation has been proposed for evaluating the effect of temperature on viscosity [13-14]:

$$\eta(T) = \eta_0 * \exp(E/RT) \qquad (4)$$

where η (T) is the viscosity as a function of temperature,
η_0 is the pre-exponential constant for viscosity,
E is the activation energy for viscosity,
R is the gas constant (8,3144 J K^{-1} mol $^{-1}$),
T is the temperature (K).

Literature (see [15-16]) offers the values of E, η_0 and η (at melting point) for some pure metals and for the Aluminium-Silicon eutectic, as described in Deliverable D2.1. For what concerns molten binary alloys, the equation proposed by Moelwyn-Hughes can be used:

$$\eta = (x_a\eta_A + x_b\eta_B) * (1 - 2\, x_a x_b \Omega\ /RT) \qquad (5)$$

where η_a and η_b are the viscosity values of the alloying elements a and b, x_a and x_b are their molar fractions, while Ω is the interaction parameter. If Ω is unknown (i.e. in the majority of cases), equation (5) can be simplified, obtaining

$$\eta = (x_a\, \eta_a + x_b\, \eta_b\,) \qquad (6).$$

For multi-component alloys, equation (6) can be generalised, achieving

$$\eta = \Sigma_i\, x_i\, \eta_i \qquad (7).$$

where i is the i-th alloying element.

This is the approach implemented into Thermo-Calc software [17], with further improvements (viscosity parameters are expanded via Redlich-Kister polynomials, fitting of activation energies, automatic conversion from kinematic viscosity, ν, to dynamic viscosity, η, via the density, ρ, of the alloy: $\nu = \eta/\rho$).
The SI unit of dynamic viscosity is pascal▪second (Pa▪s), while SI unit of kinematic viscosity is square meter per second (m^2/s).
Under these assumption, Thermo-Calc allows the viscosity to be plotted via a step calculation vs. temperature or composition. An example of the plot is given in Figure 5.

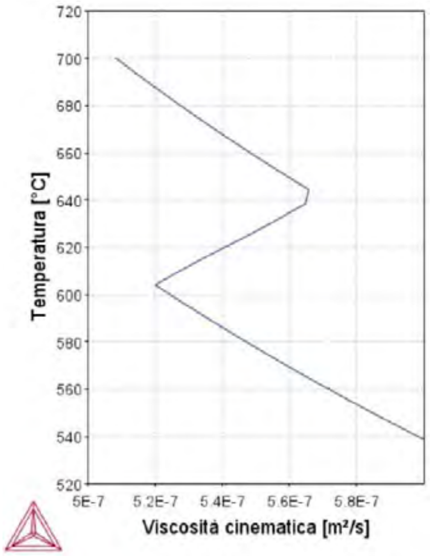
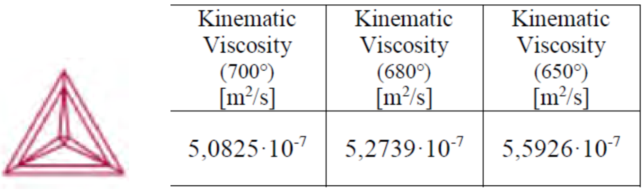


Fig. 5 – Thermo-Calc plot of viscosity as a function of temperature, for a given alloy

Thus, to have a **comprehensive overview of viscosity** (and, consequently, fluidity) of alloys depending on composition, for the various sets of alloys targeted by SALEMA, Themo-Calc modelling can be performed, and results can be extracted with reference to the relevant HPDC processing temperature range, i.e., considering 700, 680 and 650°C.

An example is given in Table 4, showing kinematic viscosity values calculated for Variant #1 of the Al-Mg system.



Kinematic Viscosity (700°) [m²/s]	Kinematic Viscosity (680°) [m²/s]	Kinematic Viscosity (650°) [m²/s]
$5{,}0825 \cdot 10^{-7}$	$5{,}2739 \cdot 10^{-7}$	$5{,}5926 \cdot 10^{-7}$

Table 4: Kinematic viscosity values calculated for Variant #1 of the Al-Mg system

3.3. Solidification shrinkage

During solidification of a metal/alloy, the density of the material changes due to cooling of the metal /alloy in both liquid and solid state as well as due to the solid to liquid phase transformation itself. Phase transformations in the solid-state during solidification may also cause a volume change which will affect the solidification process. The superheated liquid metal cools to the liquidus temperature where solidification starts. During the cooling, the melt experiences thermal contraction due to the lowered temperature. The solidification is also connected to a density change. Depending on the solidification interval of the solidifying metal, the shrinkage may occur at a specific temperature or distributed over an interval.

Solidification shrinkage may heavily impact on quality of castings, due to the possible genesis of porosity (macro-porosity, in correspondence of hot spots, or micro-porosity, when interdendritic shrinkage takes place). When HPDC is considered, solidification shrinkage is one of the most relevant causes of defects and/or imperfections, as shown in Figure 6, obtained from a survey carried out with the involvement of about 60 European HPDC foundries [18].

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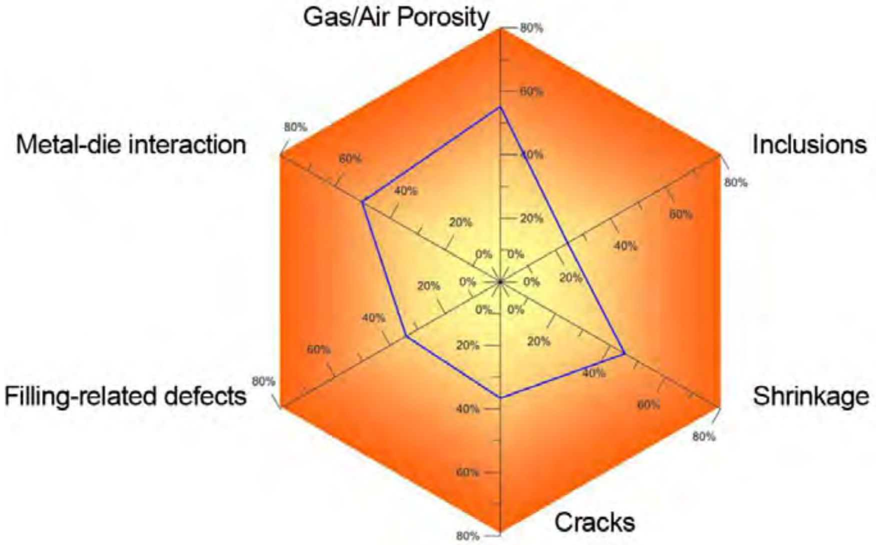

Fig. 6 – Main causes of defects/imperfections on HPDC products [18]

Thus, when designing a new alloy, an evaluation of the effect of alloying elements on solidification shrinkage is mandatory. This evaluation can be performed starting from Thermo-Calc simulations [17], followed by data elaboration.

Thermo-Calc uses a specific subroutine to evaluate the Molar Volume of alloys as a function of composition and temperature. Molar volume is the reciprocal of density multiplied by molar mass. It can be used to establish a connection with some significant physical properties, for example, viscosity, electrical conductivity and surface tension, and can be easily converted into the volume associated to a known amount of alloy (an example is shown in Figure 7).

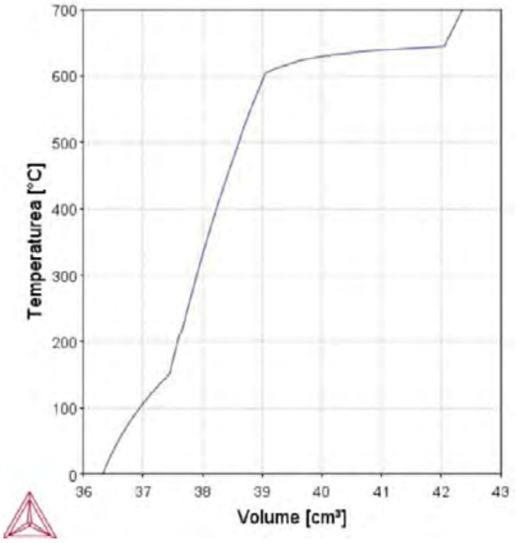

Fig. 7 – Thermo-Calc plot of volume as a function of temperature, for a given alloy

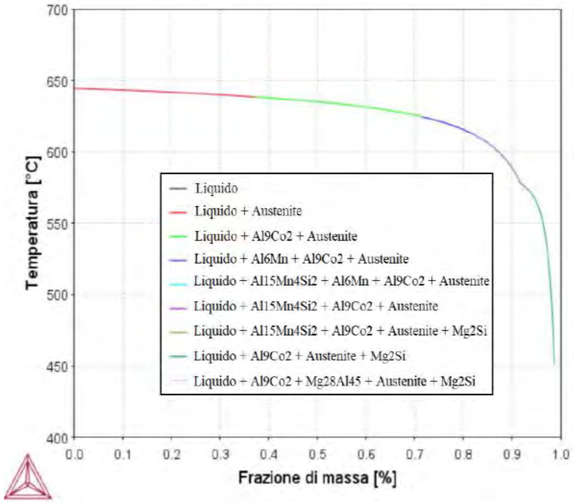

Fig. 8 – Thermo-Calc plot of equilibrium cooling curve, for a given alloy

On the other side, Thermo-Calc allows, as a “common” calculation, the determination of Liquidus and Solidus Temperatures of a give alloy, under equilibrium conditions (Figure 8).

Thus, the **procedure to be adopted** for evaluating the expected solidification shrinkage of a given alloy is the following

- Determination of Liquidus and Solidus temperatures, under equilibrium conditions, of the alloy (by Thermo-Calc),
- Determination of the corresponding values of the volume of a known amount of the alloy (by Thermo-Calc),
- Calculation of the volume change (in %) in the liquidus ➔ solidus transition (i.e. the solidification shrinkage)

3.4. Slag/dross formation tendency

Manganese and chromium are normally present in secondary Al alloys as impurities due to the recycling process of Aluminium scraps. Mn and Cr can also be intentionally added to the alloy because, singly or in combination, they neutralize the effect of Fe-needle particles by modifying the morphology and type of phase. Fe, Mn, and Cr can substitute each other in the same bcc crystal structure, α-$Al_{15}(Fe,Mn,Cr)_3Si_2$, which may appear as Chinese script, star-like or polyhedral morphology. Modification of Fe-bearing compounds with Mn and Cr addition has also some disadvantages. The complex intermetallic compounds, like primary α-$Al_{15}(Fe,Mn,Cr)_3Si_2$, have a high specific gravity and tend to segregate to the bottom of molten alloy and holding furnaces; such particles are generally called sludge. When sludge crystals are entrained into castings, they decrease the alloy's fluidity and appear as hard inclusions, which can compromise the machining operations and even more degrade the mechanical and physical properties of the component. The problem of sludge formation is often experienced in Al foundries, especially in high-pressure die-casting foundry where, in order to preserve the die and tools, the holding and casting temperatures are typical lower than in the other foundry processes (see "Inclusions" in Figure 6). Sludge formation has been shown to be dependent on the alloy's chemistry, melting and holding temperature and time. Various Authors have defined a Sludge Factor (SF) for Al-Si-Cu alloys. This factor is calculated from the Fe, Mn, and Cr contents in the alloy as follows [18]:

$$\text{Sludge Factor (SF)} = (1 \cdot \text{wt pct Fe}) + (2 \cdot \text{wt pct Mn}) + (3 \cdot \text{wt pct Cr}) \qquad (8)$$

Recently, Shabestari [19] found that the initial Fe, Mn, and Cr contents as well as the cooling rate significantly affect the morphology, amount, and size of the sludge. According to these results, the sludge forming temperature depends especially on the Fe content according to the relationship:

$$\text{Sludge Forming Temperature (°C)} = 645.7 + 34.2 \cdot (\text{wt pct Fe})^2 \qquad (9)$$

The sludge fraction depends largely on the alloy's chemistry, in particular the concentrations of Fe, Mn, and Cr, according to Eq. [8]. Various experimental investigations showed that the mean area fraction of primary Fe-rich precipitates can be plotted as a function of sludge factor, as show in Figure 9. A good fitting is given by the correlation

$$\text{Sludge fraction (wt pct)} = 1.5 \cdot \text{SF} - 1.9 \qquad (10),$$

The relationship between the SF and the holding temperature for the sludge formation is reported in Figure 10. These graphical results delineate the fields where sludge can form in AlSi9Cu3(Fe) alloys.

From the data and the correlation presented above, the **criteria and tools** to be adopted for evaluating the slag/dross formation in SALEMA alloys can be the following:

1) Evaluating, by means of Thermo-Calc simulations, the amount and temperature of formation of a-$Al_{15}(Fe,Mn,Cr)_3Si_2$-type phase
2) Evaluating SF, Sludge Forming Temperature and Sludge fraction by equations (8), (9) and (10).

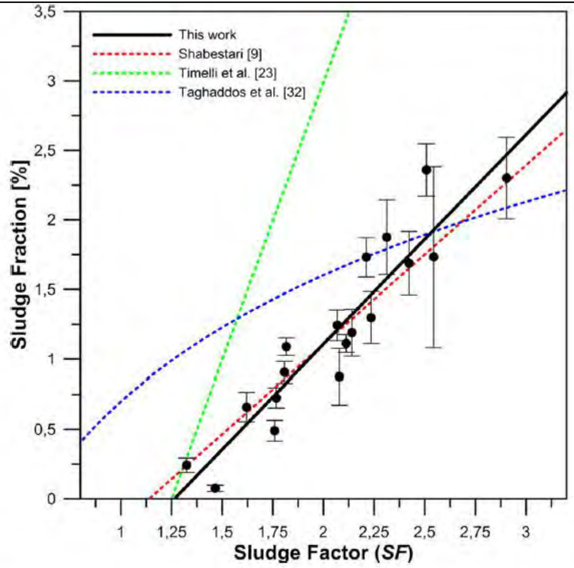

Fig. 9 – Average area fraction (pct) of sludge particles as function of Sludge Factor [18]

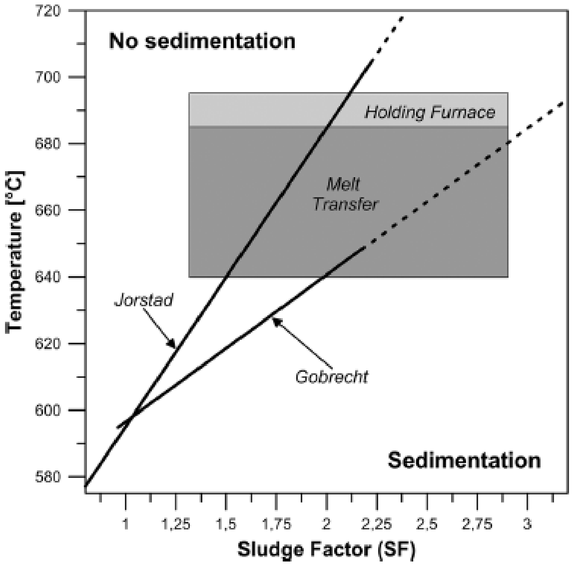

Fig. 10 – Temperature of gravity segregation of primary Fe-bearing compounds as function of the Sludge Factor in AlSi9Cu3(Fe) type alloys [18] The range of working temperatures in the holding furnace and during the melt transfer to the shoot sleeve are indicated

Results deriving from criteria #1 and #2 will be compared, in order to individuate the alloys more suitable to be investigated in HPDC tests to be performed in the context of SALEMA Project.

3.5. Die soldering tendency

Die soldering is a criticality occurring due to the formation of intermetallic layers between the tool steel and the Al-alloy (see “Metal-die interaction” in Figure 6). Such intermetallics may

- stick on the die surface (generating roughness in diecastings surface)
- stick of the diecastings surface (damaging the die surface and making easier thermal fatigue phenomena).

The combined presence of the intermetallic β-Al_5FeSi phase and a remelting region surrounding it are responsible for bonding. The intermetallic β-phase develops an irregular, needle-shaped boundary. With a solidus temperature lower than the casting temperature of the melt, the fcc-Al phase fraction of the granular layer and the AlSi-alloy become liquid in every casting cycle and solidify around the β-needles. This leads to a strong joint, and thus die soldering takes place.

The shape of the intermetallic interface can be altered by the alloy composition. Thus, die soldering can be limited by a certain content of Fe in the alloy (but this is detrimental for the casting toughness and ductility). From a general viewpoint, the optimal intermetallic interface is free of the β-Al5FeSi phase and has an evenly shaped boundary to the granular region or the AlSi-alloy. The smooth course facilitates de-molding. Additionally, the granular region should be as narrow as possible to prevent remelting. In the ideal case, the intermetallic layer should stay as a solid and compact layer on the tool steel, impeding diffusion and thus die soldering.

Manganese inhibits the formation of the β-Al_5FeSi phase. However, it creates a vast granular region. With rising Mn content, the volume fraction of intermetallic phase in the granular layer increases, while the possible remelting fcc-Al phase fraction decreases. Both effects improve the die-soldering

behaviour, yet to achieve them additions up to 0.8 wt.% are necessary. This leads to a higher proportion of brittle phases in the Al-alloy, which may decrease ductility.
Molybdenum and cobalt achieve similar effects to Mn. However, smaller additions of 0.3 wt.% are sufficient, which are presumably less harmful to ductility. While Mo presents an efficient alternative for Mn, Co seems to work only partially, with unaffected areas in between. This makes it a less-attractive solution to prevent die soldering.
Chromium is the most efficient element against die soldering. It inhibits the formation of the β-Al_5FeSi phase and reduces the overall thickness of the intermetallic interface. In addition, the granular layer becomes negligible small. Optical microscopy and EDS measurements indicate the promotion of the β -Fe_2Al_5 phase, which could impede diffusion in early states of intermetallic formation. Cr is the only element investigated, which provides both features of an optimal intermetallic interface. Addition of 0.2 wt.% of Cr, which is sufficient to achieve these effects, offers a great potential to improve the properties of AlSi-alloys over Mn. However, it must be considered that interaction between these elements may impact on ductility, as well as die-soldering prevention [20].

All these aspects can be summarised by introducing the concept that, for the casting of an Aluminium alloy in a steel die, there is a soldering critical temperature above which die soldering tends to occur [21]. The critical temperature is determined by the elements in both the casting alloy and the die material and it is the solidus temperature of the resulting dilute Aluminium alloy. At critical temperature (T_C), iron begins to react with Aluminium to form an Aluminium-rich liquid phase and solid intermetallic compounds. The liquid joins the die with the casting upon solidification. The critical temperature is determined by the elements in both the casting alloy and the die material and is equal to the solidus temperature of the resulting alloy. The critical temperature is used to predict the onset of die soldering, and the local liquid fraction is related to the soldering tendency.
Thermodynamic calculatons (e.g. by employing Thermo-Calc) can be used to determine the critical temperature and soldering tendency (Figure 11). Decreasing T_C, means increase die soldering tendency.

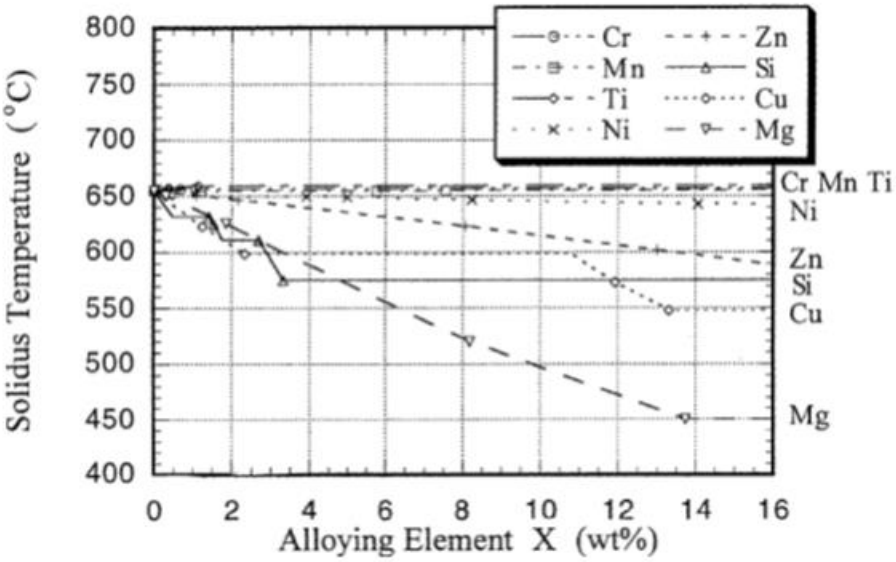

Fig. 11 – Solidus temperatures for an aluminum-4 wt pct iron-X system, in which X represents increasing amounts of alloying element X, indicating the effect of various alloying elements on the soldering critical temperature, T_C [21]

A simplified approach is offered in literature [22], with the calculation, starting from experimental test, of a die soldering index (DSI) related to selected amount of Fe, Si and Mn in the Aluminium alloy. The variation of this index is shown in Figure 12 (lower DSI numbers correspond to lower die soldering).

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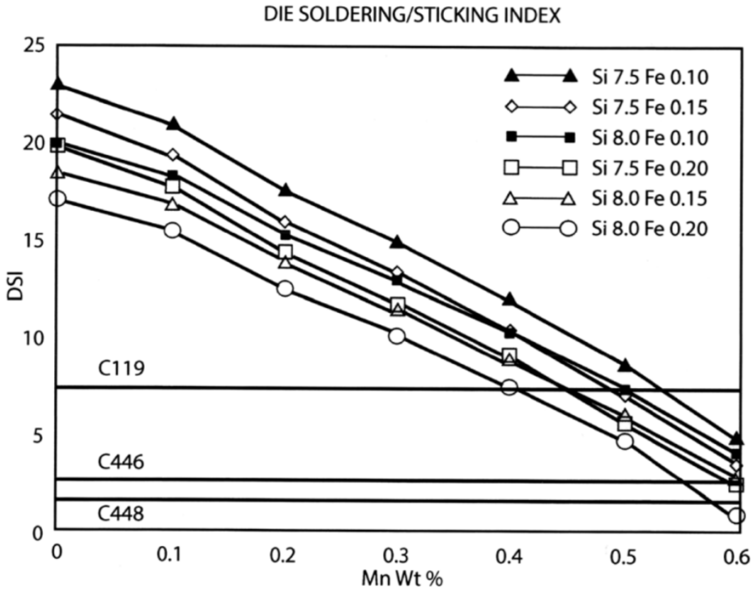

Fig. 12 – Die soldering index in several die casting alloys [22]

Another approach may be considered, by introducing the Extraction Index (EIn), which is referred directly to the amount of Fe and Mn (i.e. the elements which minimise sticking and die-soldering phenomena) in the alloy. It can be estimated as:

EIn = (wt%Fe + wt%Mn) · 100 (11).

Thus, from the data and the correlation presented above, the **criteria and tools** to be adopted for evaluating and ranking the die-soldering tendency in SALEMA alloys can be the following:

1) Evaluating, for the range of compositions where it is possible the DSI,
2) Evaluating, for all systems, the values of EIn, by equation (11)
3) Evaluating, by means of Thermo-Calc software, on a selected (from the two previous stage) group of alloys, the Critical Temperature for die-soldering

Results will be compared, in order to individuate the alloys more suitable to be investigated in HPDC tests to be performed in the context of SALEMA Project.

3.6 Hot Tearing tendency

Hot tearing is the undesired formation of irregular cracks in metal castings that develop during solidification and cooling (see “Cracks” in Figure 6), typically while the casting is still inside the die cavity. The cause of hot tearing is generally attributed to the development of thermally induced tensile stresses and strains in a casting as the molten alloy contracts during solidification and solid-state shrinkage. Hot tearing often occurs at the inside corners or fillets of casting geometries, where casting shrinkage is constrained by the relatively rigid die cavity. In fact, in die casting, the die cavity is a comparatively rigid structure (steel), in comparison to the relatively low strength Aluminium alloys, which are at high temperature. One of the key “castability” attributes considered in the development of new casting alloys is a low tendency to hot tearing.

In addition to casting design features, factors that influence hot tearing include both the casting alloy (chemical composition and solidification characteristics), and casting process parameters. Therefore, hot tearing tends to be of greater concern in die casting processes, compared to sand casting processes where the mould cavity is typically lower in strength, and more compliant to casting shrinkage. Hot tearing cracks can be seen, experimentally, using Hot Cracking Indexing (HCI) test (Figure 13).

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Fig. 13 – 3D-picture of dog bone shaped sand casting for HCI evaluation [23]

It is generally accepted that as the freezing range increases, the hot cracking susceptibility also increases. Depending on cooling conditions, a long freezing range leads to the formation of complex dendrites which interlock at relatively low fraction of solid to form rigid bridges. Subsequently, feeding at the late stages of solidification is greatly hindered. Because pure metals and eutectic alloys have little to no freezing range, they show no hot cracking susceptibility. The chemical composition is the main influencing factor on the freezing range [23]. Impurities and their segregations which increase the freezing range are deleterious. Correlations among alloy composition, freezing range and hot cracking tendency are displayed in Figure 14 [24].

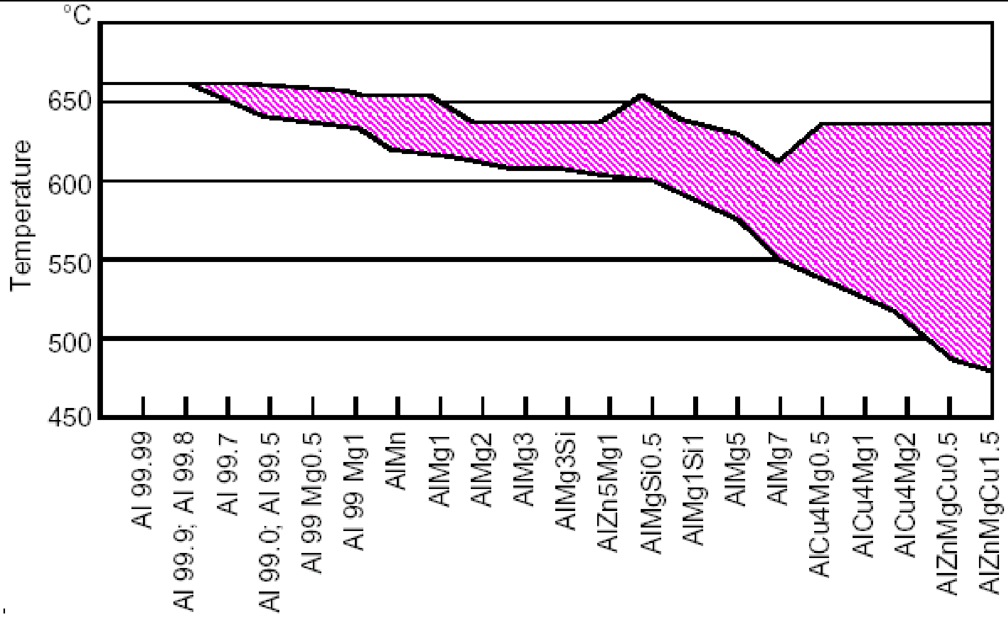


Fig. 14a – Freezing range of various Aluminium alloys [24]

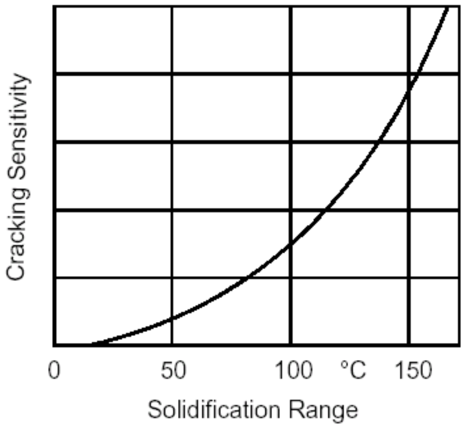


Fig. 14b – Hot tearing sensitivity as a function of solidification range [24]

Furthermore, the final freezing range, the so-called terminal freezing range (TFR), is of major importance. A large TFR causes a higher risk of hot cracks in the last stage of solidification. If in an eutectic system a large amount of dendrites is formed already well above the solidus (i.e. at high temperature), the alloy possesses a high strength during final solidification of the remaining liquid, resisting contractional stresses. For alloys close to eutectic composition, large amounts of liquid freeze isothermally at the eutectic temperature (i.e. at low temperature) and shrinkage stresses are kept small. It has been suggested [23] to evaluate TFR in temperature intervals of mass fraction solid as 95-99.5% (Figure 15). The very last percentage is neglected because of susceptibility to errors.

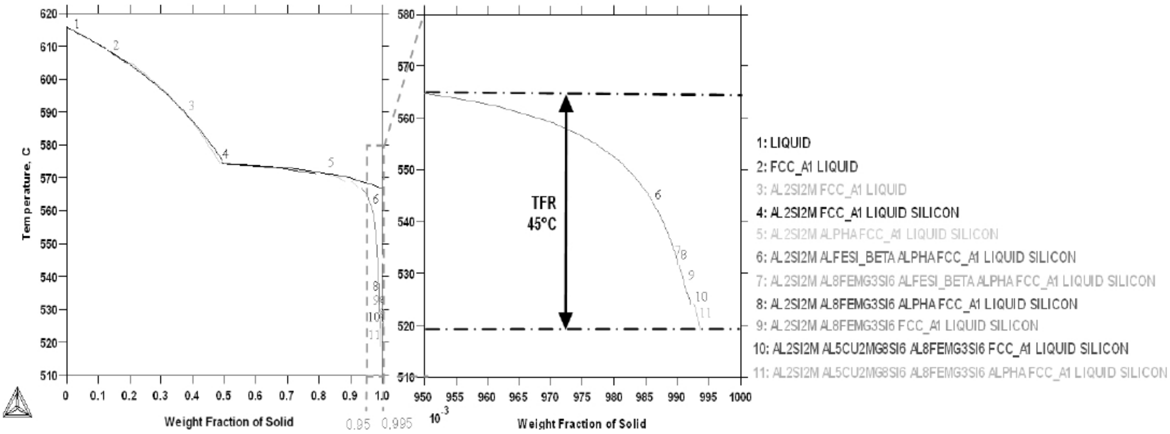


Fig. 15 – Example of TFR calculation for (AlSi7Mg0.1Cu0.5 alloy) [23]

Thus, from the data and the correlation presented above, the criteria and tools to be adopted for evaluating and ranking the hot tearing tendency in SALEMA alloys can be the following:

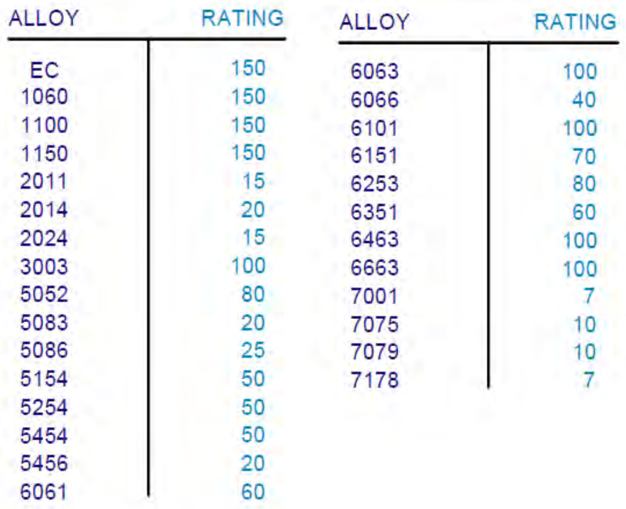
- Calculation of TFR by the software Thermo-Calc; for simulation of the solidification process, existing phases and their fraction at the different temperatures can be estimated for non-equilibrium using Gulliver-Scheil approach [17]
- Defining hot tearing tendency as directly proportional to the amplitude of TFR.

4. Criteria & tools to evaluate hot working attitude and extrudability

4.1 The concept of extrudability

All aluminium alloys can be extruded or stamped, but some are less suitable than others, requiring higher pressures, allowing only low deformation speeds and/or having less than acceptable surface finish and section complexity. Thus, while large quantities of pure aluminium are extruded for production of electrical conductors, strong alloys in the 2000, 7000 and 8000 series used for spars and stringers in airframe construction and large sections in the 5000 series employed in marine structures, the biggest share of the extrusion market is taken by the 6000, AlMgSi series. From a general viewpoint, Aluminium alloys can be considered as a set of materials ranging in strength from 150 MPa to 350 MPa, all with good toughness and formability. They can be extruded with ease and their overall "extrudability" is good. Alloys containing the lower limits of Magnesium and Silicon e.g. 6060 and 6063 extrude at very high speeds - up to 100 m/min with good surface finish, anodising capability and maximum complexity of section shape combined with minimum section thickness. For these reasons, such group of alloys is often taken as a reference when an "extrudability" index is used to embrace all these issues with pure aluminium at one end of the scale and the strong aluminium/zinc/magnesium/copper alloys on the other. Alloy selection is important because it establishes the minimum thickness for a shape and has a basic effect on extrusion cost. Because of the mentioned complex interaction of process factors this rating can be seen only for guidance. Tables 5a-b show, according to different Authors [25-26], the relative extrudabilities, as measured by extrusion rate, for several of the more important commercial extrusion alloys. Table 6 shows similar results, but presenting an index referred to difficulty in extrusion.

It is also clear (and shown in Figures 16-17) that extrudability is inversely proportional to the yield strength of the alloys.



ALLOY	RATING	ALLOY	RATING
EC	150	6063	100
1060	150	6066	40
1100	150	6101	100
1150	150	6151	70
2011	15	6253	80
2014	20	6351	60
2024	15	6463	100
3003	100	6663	100
5052	80	7001	7
5083	20	7075	10
5086	25	7079	10
5154	50	7178	7
5254	50		
5454	50		
5456	20		
6061	60		

Table 5a – Example of Extrudability Index of various Aluminium alloys [25]

Alloy	Extrudability (% referred to AA6063)
1350	160
1060	135
1100	135
3003	120
6063	100
6061	60
2011	35
5086	25
2014	20
5083	20
2024	15
7075	9
7178	8

Table 5b – Example of Extrudability Index of various Aluminium alloys [26]

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Alloy	*Difficulty*	*Alloy*	*Difficulty*
1000	77	3004	180
1100	86	6082	197
6063	100	2014	202
3005	106	5052	229
3003	112	5056	232
6105	134	2024	247
4047	128	5054	265
3105	126	7150	269
6061	151	7050	280
5005	154	5083	281
7004	157	5182	293
2011	171	5456	300
		7075	316

Table 6 – Comparison of the relative extrudability of Al-alloys [27]

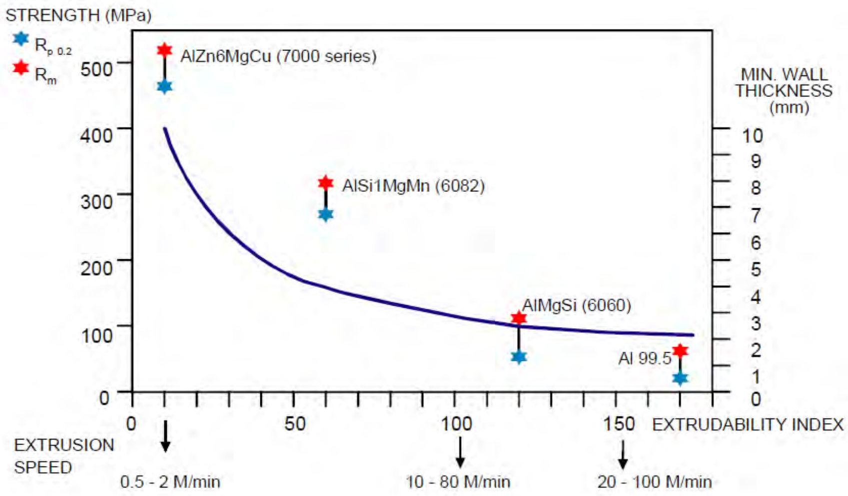
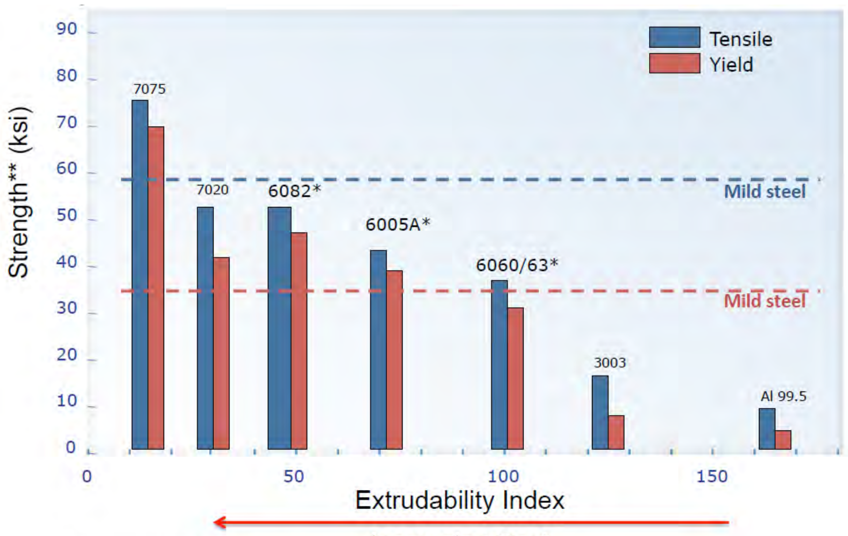


Fig. 16 – Extrudability Index, typical extrusion speed, strength and minimum wall thickness achievable for various Aluminium alloys [25]



* T6, except 6005A @ T61
**typical properties

Fig. 17 – Example of Extrudability Index of various Aluminium alloys

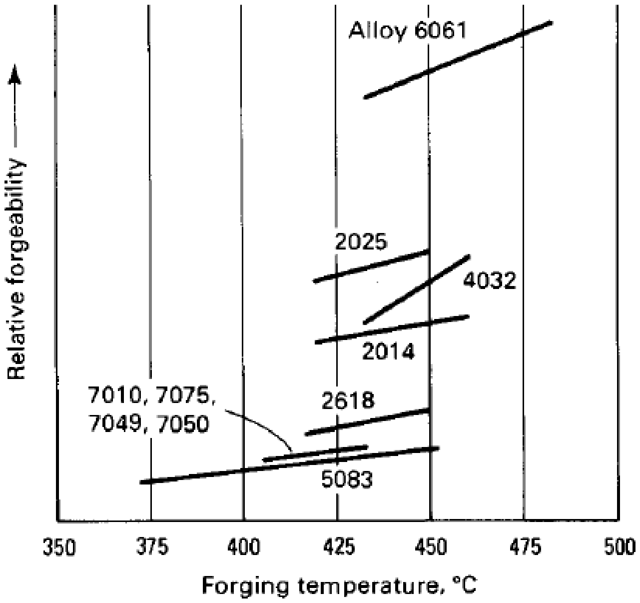


Fig. 18 – Forgeability and forging temperatures of various Aluminium alloys [26]

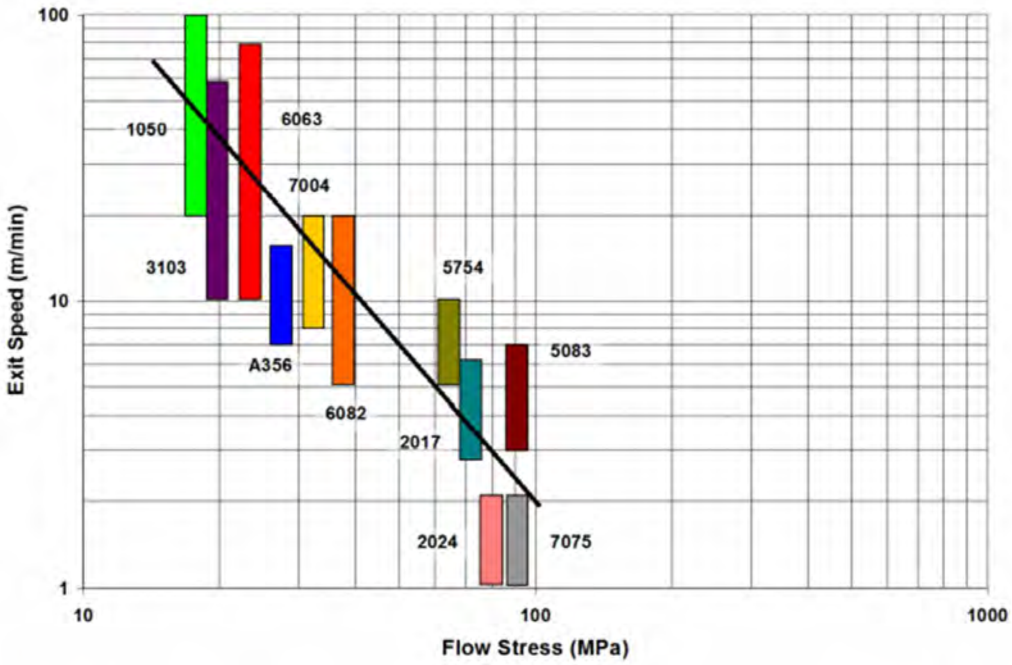


Fig. 19 – Correlation between flow stress and extrusion speed for various alloys [28]

Similar considerations can be done if forging and stamping processes are considered, as shown in Figure 18, showing relative forgeability of various Aluminium alloys [26].

Furthermore, it has to be considered that extrudability (and thus attitude to hot deformation) can be related to the flow stress of the alloys, as shown in Fig. 19. When the alloy is hot deformed, the main contribution to its resistance (i.e. to its flow stress) is constituted by solid solution strengthening.

4.2 Criteria for evaluating attitude to hot working (extrusion, stamping) in wrought alloys

A general remark, directly resulting from previous section, is that the higher the alloy content and the strength of an alloy, the more difficult it is to extrude and the lower its extrusion rate. This concept can be easily understood considering that, at the extrusion and/or forging and/or stamping temperature, the resistance to deformation (i.e. the difficulty in hot working) can be related to the yield strength of the alloys, which, at that temperature, is associated only to the solid solution strengthening mechanism.

Furthermore, it is well-known that solid solution strengthening is directly related to the content of alloy elements, as shown by Hall-Petch law:

$$\sigma_s = \sigma_i + kd^{-\frac{1}{2}} + \sum_{1}^{n} C_i(\%X_i) \tag{11}$$

where σ_i and k are constants related to Aluminium, d is the grain size, C_i is contribution to strength of the i-th alloying element and $\%X_i$ is its content.

This phenomenon is shown in Figure 20, where the correlation among alloying elements (Cu, Mg, Mn, Si and Zn) and extrudability is assessed.

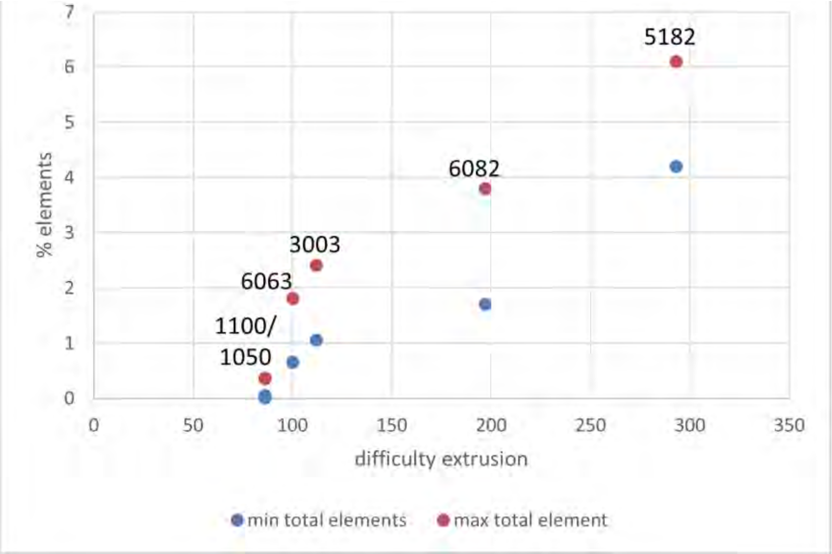


Fig. 20 – Correlation among alloying elements (Cu, Mg, Mn, Si and Zn) and extrudability

Element	**Temperature for maximum solubility [°C]**	**Maximum solubility [wt%]**
Cu	548	5.65
Fe	655	0.05
Li	600	4.20
Mg	450	17.40
Mn	658	1.82
Si	577	1.65
Zn	443	70.00

Table 7 – Temperature at which maximum solubility is achieved and the related values for key-alloying elements in Aluminium [26]

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Element	**Maximum solubility [wt%]**
Ag	55.60
Cr	0.77
Ti	1.00
Zr	0.28

Table 8 – Maximum solubility for some alloying elements in Aluminium [26]

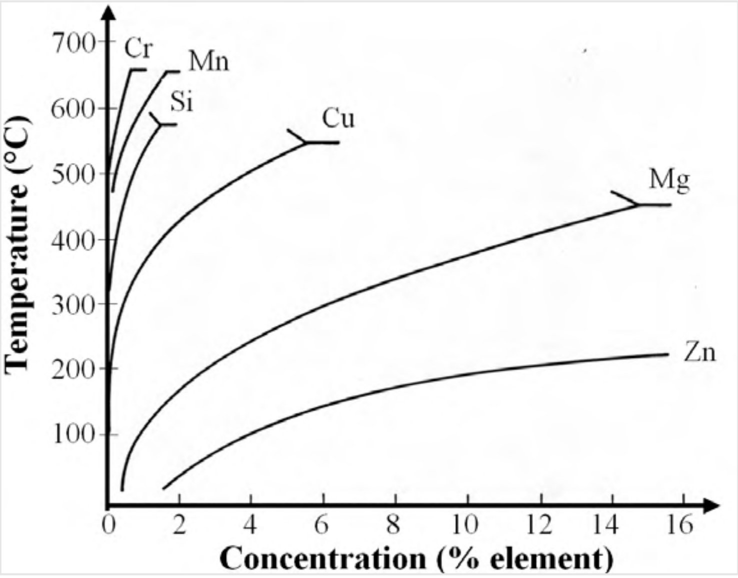

Figure 21 – Solubility curves of key-alloying elements in Aluminium [26]

Thus, in view of prediction of attitude to hot deformation of alloys (i.e. attitude to extrusion and rolling), a simplified approach should be that of using the amount of alloying elements as the reference parameter. Figure 21 describes the solubility curves of key-alloying elements in Aluminium, while Tables 7-8 reports the temperature at which maximum solubility is achieved and the related values.

Thus, from the data and the correlation presented above, the **criteria and tools** to be adopted for evaluating and ranking attitude to hot workability in SALEMA alloys can be the following:

- Developing and/or individuating simplified models based on solid solution strengthening as a function of alloys composition (from Table 7, at processing temperature, all alloying elements are expected to be in solid solution)
- Applying these models to a wide set of compositions (subject of Deliverable D2.3),
- Selecting the specific systems offering the (theoretical) best set of attitudes to hot working (subject of Deliverable D2.3),
- Performing experimental campaigns to verify "in field" the optimal solutions, to be finally implemented in industrial production (subject of Deliverable D2.4).

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5. Criteria & tools for mechanical compensation of Si and Mg decrease in alloys

5.1. Role of Mg and Si on alloys performance

The major strengthening mechanisms for Al-alloys are precipitation strengthening, solid solution strengthening, grain boundary strengthening and work hardening. They are not acting all together, due to the peculiarity associated to alloy specific compositions and to processes. If alloys containing Si and/or Mg are considered, the situation is described in Table 9. If the amount of Si and Mg is addressed in terms of minimisation, some aspects are worth mentioning:

- minimisation can be performed even in the frame of the same alloy class (see Figure 22),
- strategies to be adopted to achieve adequate "mechanical compensation" are different, according to the strengthening mechanism considered.

Various models and tools are offered by literature to evaluate how to "mechanically compensate" the decrease of Si and Mg, and will be reported in next sections, in view of their application in designing SALEMA low CRM alloys.

Strengthening mechanism	**Casting alloys**		**Wrought alloys**	
	Al-Mg	**Al-Si-Mg**	**5000 (Al-Mg)**	**6000 (Al-Mg-Si)**
Solid solution	√	√	√	√
Grain refinement	√	√	√	√
Precipitation		√		√
Work hardening			√	

Table 9 – Strengthening mechanisms in Aluminium alloys

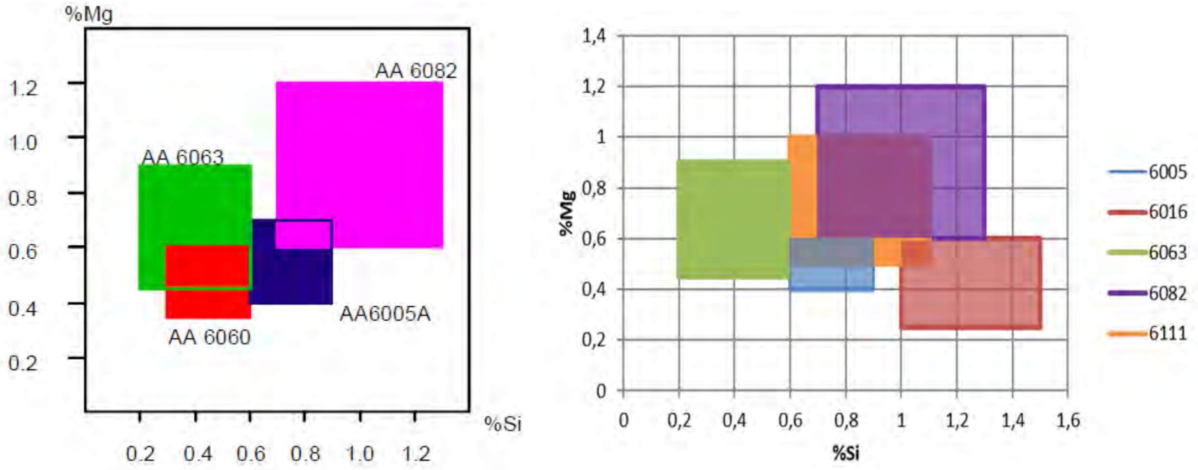

Fig. 22 – Visualisation of composition range for the most common 6000 alloys [31]

5.2. Models for solid solution strengthening

Solute atoms, whether interstitial or substitutional, strengthen the matrix primarily due to the variation in their size, modulus and valency. The degree of strengthening depends on the concentration of solute atoms, and can be expressed using one of the following equations [30-32]

$$\Delta\sigma_{ss} = \sum_{j} k^{j} C_{i}^{j\frac{2}{3}} \qquad (11),$$

or, alternatively, as

$$\Delta\sigma_{ss} = \sum_{j} k^{j} C_{i}^{j} \qquad (12),$$

where $\Delta\sigma_{ss}$ is the solid solution strengthening in MPa, k^i is the scaling factor for the j^th^ element and C_i^j is the concentration in weight of the jth solute in the matrix. The specific values of k^i to be implemented in equations (11) and (12) are collected in Table 10.

Element	**Difference in atomic radii (%) with Al**	**Yield strength/ % addition**		**Tensile strength/ % addition**	
		MPa/at%	**MPa/wt%**	**MPa/at%**	**MPa/wt%**
Si	-3.8	9.3	9.2	40.0	39.6
Zn	-6.0	6.6	2.9	20.7	15.2
Cu	-10.7	16.2	13.8	88.3	43.1
Mn	-11.3	n.a.	30.3	n.a.	53.8
Mg	+11.8	17.2	18.6	51.0	50.3

Table 10 – Solid-solution effects on strenght of principal solute elements in super purity Aluminium

Thus, on the basis of composition, **the criteria and tool to calculate $\Delta\sigma_{ss}$** for each candidate alloy are

- Evaluation of expected content of solid solution elements, by means of Themo-Calc software or by existing equilibrium diagrams,
- Applying equations **(11)** and/or **(12)**, with implemented amount of solute elements and coefficients reported in Table 10.

5.3. Models for grain refinement (grain boundary) strengthening

The grain boundary strengthening of a polycrystalline material is evaluated using the well-known Hall-Petch relation:

$$\Delta\sigma_{gb} = \sigma_{i} + k_{i} d^{-\frac{1}{2}} \qquad (13),$$

where $\Delta\sigma_{gb}$ is the increase in yield strength due to grain boundary strengthening, σ_i is the intrinsic strength (against dislocations movement) at infinite grain size, k_i is the locking factor and d is the grain size in micron. Typical values of σ_i and k_i for Al-alloys are 16 MPa and 0.065 MPa·m$^{-1/2}$, respectively.
The control of grain size (and thus of mechanical properties) is associated, in some cases, to composition (e.g. it is well-known the role of Ti as grain refiner), in some others to processing conditions (e.g. deformation parameters and temperature in rolling and extrusion, or cooling rate in castings, as already discussed in Deliverable D2.1).

In the frame of SALEMA project, the following **criteria and tools** will be used for taking into account grain refinement effects on alloys mechanical performance (also in terms of mechanical compensation of Si and Mg decrease):

- possible use of Ti as micro-alloying element,
- estimation of typical grain size ranges associated to reasonable processing (casting, extrusion, rolling & stamping) conditions,
- evaluation of related effects on mechanical behaviour by means of equation (13).

5.4. Models for precipitation hardening

The classical attempts to predict the precipitation strengthening is based on interaction between spherical shaped particles and dislocations. In AA6063 Al–Mg–Si alloy, the precipitates are of rod shaped and models incorporating this particle shape are also proposed by various researchers [29-30, 32-33]. These models consider various modifications of Orowan equation, thermodynamics for precipitation and diffusional transformation with appropriate consideration of temperature and time. The latter considerations can provide estimation of the volume fraction of the transformed precipitates and their radius [32-33]. A brief account of these models is summarized below preceded by an outline of the conventional strengthening mechanisms which remain inherently associated with the former ones.

In the case of Classical dislocation-particle interaction model, the increase in YS due to precipitation hardening can be described by the following correlation:

$$\Delta\tau_{\mathrm{ppt}} = \frac{1}{br}\left(2\beta G b^2\right)^{-\frac{1}{2}}\left(\frac{3f}{2\pi}\right)^{\frac{1}{2}} F^{\frac{3}{2}} \qquad (14),$$

In the case of Non-shearable particle model, the following correlation describes the increase in YS due to precipitation hardening:

$$\Delta\tau_{\mathrm{ppt}} = 0.\,13\frac{Gb}{L}\ln\frac{r}{b} \qquad (15),$$

Full description and comments concerning the terms and symbols adopted in correlations (14) and (15) are reported in Refs [29-30].

Finally, the overall increase of YS due to the contribution of all strengthening mechanisms can be estimated by

$$\sigma_{\mathrm{ys}} = \Delta\sigma_{\mathrm{ss}} + \Delta\sigma_{\mathrm{gb}} + M\sqrt{\left(\Delta\tau_{\mathrm{ms}}{}^2 + \Delta\tau_{\mathrm{ppt}}{}^2\right)} \qquad (16),$$

with all symbols and terms reported in Refs [29-30].

When the effect of precipitation hardening on Al-Si-Mg systems is addressed, some issues are worth mentioning.

First of all, every change in amount of Si and Mg results in modification of solutioning (i.e. the first processing stage of the precipitation hardening treatment) temperature, as well as in the amount of Mg_2Si precipitates achieved after ageing treatment and, consequently, in final mechanical behaviour. This situation is described in Figure 23.

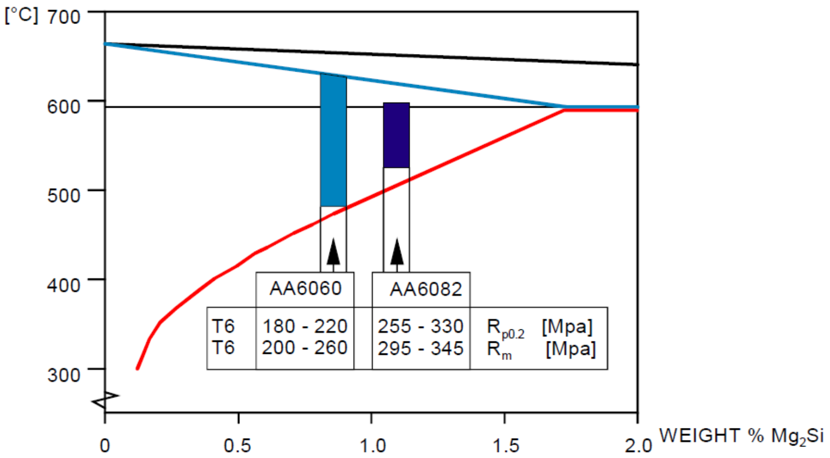

Fig. 23 – Change in solutioning temperature and in mechanical properties due to variation in Mg and Si content [31]

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A second issue concerns the fact that different processing solutions can be applied in precipitation hardening heat treatments. These solutions are associated to the adoption of the following options:

T4: solution heat treatment and naturally aged,
T5: cooled and artificially aged,
T6: solution heat treatment and artificially aged,
T7: solution heat treatment and artificially overaged or stabilised.

These heat treatment solutions lead to different amount, size, distribution of the reinforcement phase Mg_2Si, which practically means that different combinations of elongation, YS and UTS can be achieved by the treated alloy. This concept is well visualised in Figure 24 (referred to diecasting alloys) and in Figure 25, referred to 6000 wrought alloys,

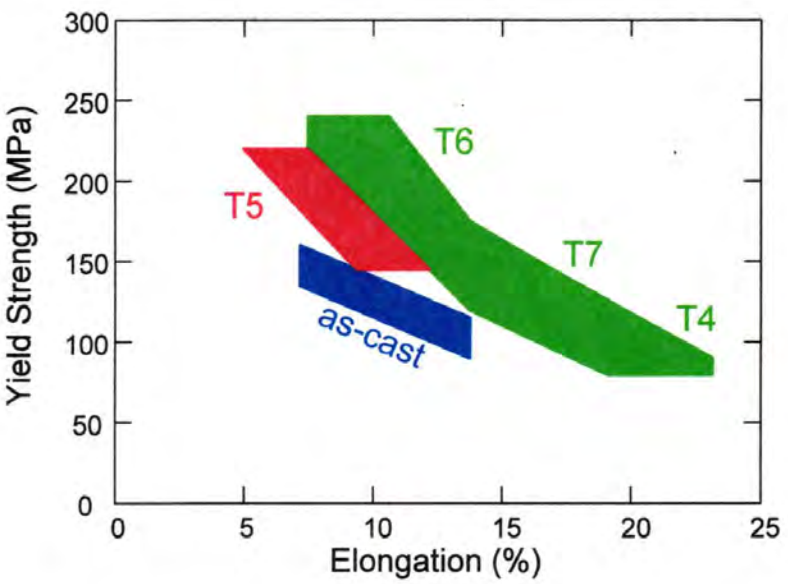

Fig. 24 – Range of properties available in structural diecastings, as a function of heat treatment [22]

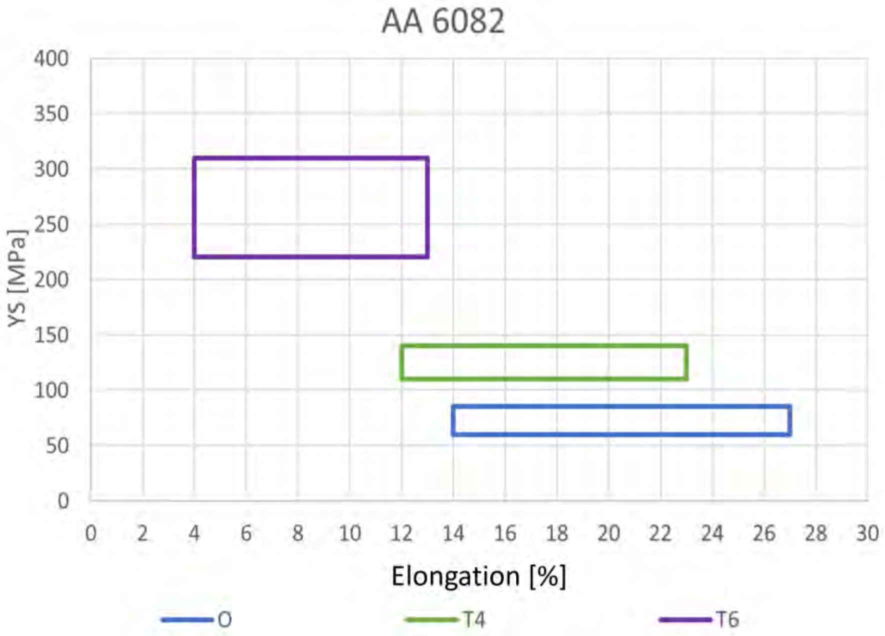

Fig. 25 – Mechanical properties of 6082 alloy, as function of its metallurgical state [31]

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The third issue is that models summarised by correlations (14) and (15) can be successfully used [29-30] to estimate the effect that temperature of ageing (TA) and time of ageing (tA) play on fraction, average size, characteristics of precipitates. Consequently, via the application also of equation (16), the final yield strength of alloys, associated to active key-strengthening mechanisms, can be estimated. This approach is usually known as the elaboration process maps, and is well illustrated in Figure 26, correlating temperature of ageing (TA), time of ageing (tA) and yield strength of AA6063 alloy.

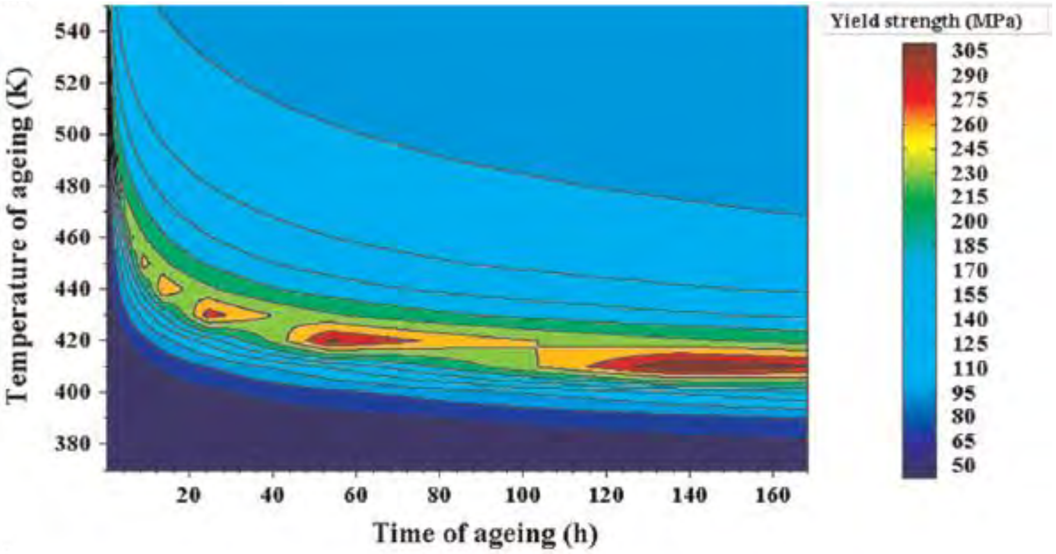

Fig. 26 – Example of process maps illustrating the correlation amongst temperature of ageing (TA), time of ageing (tA) and yield strength of AA6063 alloy [29]

For the purpose of optimisation of SALEMA alloys, all these information can be usefully taken into account. In fact, **models and tools** to elaborate process maps for some selected alloys systems can be developed and used to define the best processing conditions (to be tested in experimental campaigns) to achieve the requirements individuated for SALEMA Demonstrators.

5.5. Models for work hardening

In the context of Al-alloys systems addressed by SALEMA Project, the strengthening effect due to work hardening mechanism is associated to 5000 (i.e. Al-Mg) alloys.

According to the metallurgical state of the alloys, related to the deformation grades applied in various processing stages, different combination of elongation and yield strength can be achieved, as described in Figure 27, showing mechanical properties of 5754 alloy, as function of its metallurgical state. In other terms, also in the case of work hardening strengthening mechanism, an approach based on process maps can be introduced. Figure 27, describing the role of different work hardening levels on elongation and YS, represent a process map for 5754 alloy.

Consequently, for the purpose of optimisation of SALEMA alloys, when work hardening strengthening mechanism is involved, the **elaboration of process maps** can be targeted for some selected alloys systems. Process maps can be used to define the best processing conditions (to be tested in experimental campaigns) to achieve the requirements individuated for SALEMA Demonstrators.

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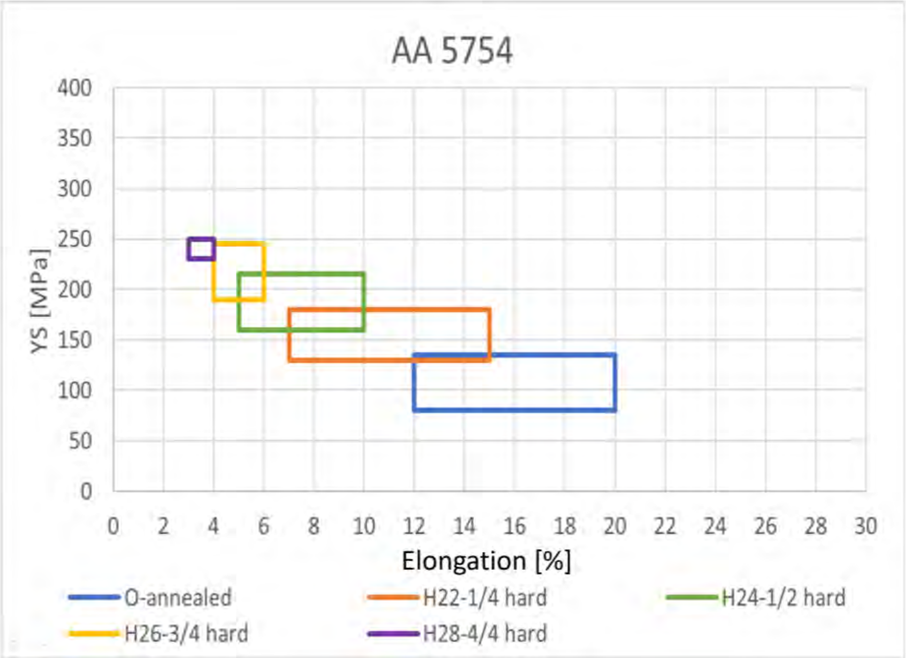

Fig. 27 – Mechanical properties of 5754 alloy, as function of its metallurgical state [31]

6. Summary of Criteria and Tools for exploring alternative alloying systems

Previous Chapters described theoretical and literature basis supporting the development of criteria and tools, to be used for exploring alternative alloying systems in view of the achievement the best possible compromise among low content of CRM, adequate processability and good performance.
These criteria and tools, which will be implemented in D2.3 for defining specific alloys for experimental investigations, are summarised below.

CRITICALITY

EVALUATION OF CRITICALITY INDEX

Excel database containing information about alloy designation, condition, and chemical composition; elements that are critical, based on European Commission resolution, and the corresponding value of the overall criticality index are collected. The CI_A assessment for a specific alloy can be achieved simply by inserting its composition, in such excel file.

CASTABILITY

VISCOSITY

Viscosity (and, consequently, fluidity) of alloys depending on composition, are evaluated by Themo-Calc modelling; results can be extracted with reference to the relevant HPDC processing temperature range, i.e. considering 700, 680 and 650°C.

SOLIDIFICATION SHRINKAGE

Expected solidification shrinkage can be calculated by
- Determination of Liquidus and Solidus temperatures, under equilibrium conditions, of the alloy (by Thermo-Calc),
- Determination of the corresponding values of the volume of a known amount of the alloy (by Thermo-Calc),
- Calculation of the volume change (in %) in the liquidus-solidus transition (i.e. the solidification shrinkage)

SLAG/DROSS FORMATION TENDENCY

Slag/dross formation tendency can be estimated by
- Evaluating, by means of Thermo-Calc simulations, the amount and temperature of formation of α-$Al_{15}(Fe,Mn,Cr)_3Si_2$-type phase
- Evaluating SF, Sludge Forming Temperature and Sludge fraction by equations (8), (9) and (10)

Results deriving these criteria must be compared, in order to have a balanced view of alloy behaviour.

DIE SOLDERING TENDENCY

Evaluation and ranking of the die-soldering tendency can be performed by
- Evaluating, for the range of compositions where it is possible the DSI,
- Evaluating, for all systems, the values of EIn, by equation (11)
- Evaluating, by means of Thermo-Calc software, on a selected (from the two previous stage) group of alloys, the Critical Temperature for die-soldering

HOT TEARING TENDENCY

Evaluation and ranking of hot tearing tendency can be performed by
- Calculation of TFR by the software Thermo-Calc (existing phases and their fraction at the different temperatures estimated for non-equilibrium using Gulliver-Scheil approach [17])
- Defining hot tearing tendency as directly proportional to the amplitude of TFR.

HOT WORKING ATTITUDE AND EXTRUDABILITY

Hot Workability

Evaluation and ranking of attitude to hot workability can be estimated by simplified models based on solid solution strengthening as a function of alloys composition, considering that, at processing temperature, all alloying elements are expected to be in solid solution

MECHANICAL COMPENSATION OF Si AND Mg DECREASE IN ALLOYS

Solid Solution Strengthening

$\Delta\sigma_{ss}$ for each candidate alloy can be estimated by

- Evaluation of expected content of solid solution elements, by means of Themo-Calc software or by existing equilibrium diagrams,
- Applying equations [Y] and/or [Y], with implemented amount of solute elements and coefficients reported in Table 9.

Grain Refinement

For taking into account grain refinement effects on alloys mechanical performance (also in terms of mechanical compensation of Si and Mg decrease), the strategy is:

- possible use of Ti as micro-alloying element,
- estimation of typical grain size ranges associated to reasonable processing (casting, extrusion, rolling & stamping) conditions,
- evaluation of related effects on mechanical behaviour by means of equation (13).

Precipitation Hardening

Process maps can be elaborated for some selected alloys systems and used to define the best processing conditions (to be tested in experimental campaigns) to achieve, by proper tuning, the requirements individuated for SALEMA Demonstrators.

Improving Work Hardening

Process maps can be elaborated for some selected alloys systems and used to define, by proper tuning, the best processing conditions (to be tested in experimental campaigns) to achieve the requirements individuated for SALEMA Demonstrators.

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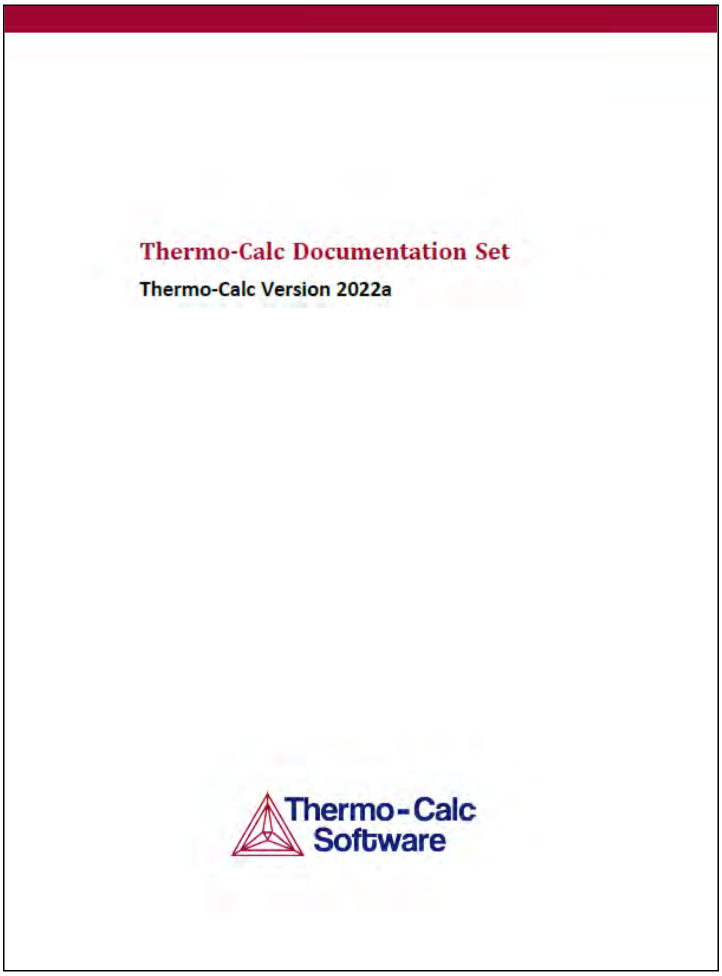
Annex 1

Themo-Calc Software

Thermo-Calc Software develops computational tools used to predict and understand materials properties, allowing generation of computational materials data without costly, time-consuming experiments or estimations based on the limited data available. It can be used to fill the gaps in material property data and make predictions of material behaviour throughout the materials life cycle. The Thermo-Calc software (also referred to as the Thermo-Calc program or the software to distinguish it from the company name) is used to perform thermodynamic calculations. It can calculate complex homogeneous and heterogeneous phase equilibria, and then plot the results as property diagrams and phase diagrams. The software fully supports stoichiometric and non-ideal solution models and databases. These models and databases can be used to make calculations on a large variety of materials such as steels, alloys, slags, salts, ceramics, solders, polymers, subcritical aqueous solutions, supercritical electrolyte solutions, non-ideal gases, and hydrothermal fluids or organic substances. The calculations take into account a wide range of temperature, pressure, and compositions conditions.



Thermo-Calc Documentation Set

Thermo-Calc Version 2022a

Thermo-Calc
Software