Alberto Fabrizi, Giulio Timelli, Stefano Ferraro, Franco Bonollo
Department of Management and Engineering, University of Padua, Vicenza, Italy

Evolution of Fe-rich compounds in a secondary Al–Si–Cu alloy: influence of cooling rate

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The influence of cooling rate on the chemical composition and morphological structure of Fe-rich intermetallics in a secondary Al–Si–Cu alloy has been investigated by using several analysis techniques such as optical microscopy, scanning electron microscopy, energy dispersive spectroscopy and backscattered electron diffraction. Morphological, chemical composition and size evolution of α-Al(Fe,Mn,Cr)Si have been observed and characterized under different solidification conditions. By varying the cooling rate, α-Al(Fe,Mn,Cr)Si blocky crystals, as well as chinese-script, branched structures and dendrites form, while coarse β-Al(Fe,Mn)Si needles appear at lower cooling rates.

Keywords: Al–Si–Cu alloy; Fe-rich phases; Cooling rate; Solidification; Microstructure

1. Introduction

Among the different Al foundry alloys used for automotive applications, recycled (or *secondary*) Al–Si–Cu casting alloys have seen increasing demand in recent years.

Generally, the aluminium produced from recycled metal saves about 90 % of the energy required for primary aluminium production. Metal recycling is a convenient process from an eco-sustainability point of view; indeed, the secondary Al process creates about 5 % of the CO_2 produced by primary Al route [1]. Due to the energy-saving and the reduction of dependence on overseas sources, increasing the amount of recycled metal represents a key factor for mechanical and transport industries.

Industry also has to pay particular attention to the quality of recycled Al alloys, being a requirement for the production of high performance components. Therefore, control of impurities and inclusions is a fundamental technological aspect of the secondary Al industry.

Iron is largely considered the principal impurity and harmful alloying element for Al–Si–Cu alloys. The presence of iron promotes the precipitation of Fe-rich intermetallic compounds having deleterious effects on the mechanical properties as well as castability and machinability. In high pressure die casting (HPDC) of Al–Si–Cu alloys, Fe-rich compounds can assume different morphologies such as needle-like, chinese-script and star-like or polyhedral morphology [2, 3]. Commonly, the needle-like compounds are identified as monoclinic Al_5FeSi phase (β-Fe) while chinese-script and compact particles are identified as $Al_{15}(Fe,Mn)_3Si_2$ or $Al_{12}(Fe,Mn)_3Si$ phase (α-Fe) with a body centred cubic (bcc) crystal structure [4]. Due to their acicular morphology, the β-Fe particles are considered more detrimental than α-Fe phases [5, 6].

According to the literature [7–9], the nature of the phase, the morphology, size and fraction of the Fe-rich compounds are influenced by the initial alloy chemical composition and the solidification history. It has been found that the Fe, Mn and Cr levels, as well as their reciprocal ratios, can affect the morphology of the Fe-rich compounds: high Fe : (Mn + Cr) ratio usually favours the precipitation of needle-like particles whereas a larger amount of chinese-script and/or polyhedral, star-like and blocky particles is achieved for a ratio lower than 2.

Besides the chemical composition, the cooling rate contributes to determining the nature of the Fe-rich phases due to the variation of diffusion and solubility coefficients of the atoms during the solidification process [10, 11]. An increase in the cooling rate can lead to the inhibition of β-Fe formation and to the promotion of α-Fe precipitation [12].

In this work, the evolution of morphology and chemical composition of α-Fe phase in a secondary Al–Si–Cu alloy was studied as function of the cooling rate by using different investigation techniques.

2. Experimental procedure

2.1. Base material

The base material used in this investigation was prepared by mixing in suitable proportion a commercial secondary AlSi9Cu3(Fe) cast alloy, supplied as commercial ingots, with three different master alloys, Al-25Fe, Al-25Mn and Al-10Cr respectively. After the addition of the master alloys, the melt was heated in a gas-fired crucible furnace at 760 ± 5 °C and held for at least 30 minutes to ensure homogeneity and dissolution of intermetallics. The chemical composition of the resultant alloy, measured on separately poured samples, is reported in Table 1.

Specimens of the base material were then produced by means of a cold chamber high pressure die casting machine: a complete description of HPDC process parameters is published in Ref. [13]. Such specimens were then used for the further experimental tests.

Table 1. Chemical composition of the experimental alloy (wt.%); *SF* = sludge factor.

Si	Cu	Fe	Mn	Cr	Mg	Zn	Ni	Ti	Al	Fe : (Mn + Cr)	*SF*
8.20	2.388	1.42	0.59	0.10	0.207	1.019	0.053	0.037	bal.	2.06	2.90

2.2. Melting and cooling conditions

In order to evaluate the influence of the cooling rate on the morphology and chemical composition of the Fe-rich compounds, several pieces (80 g each) were drawn from the diecast specimens, remelted inside an alumina crucible (inner diameter of 20 mm and height of 80 mm) by using an electric-resistance muffle furnace and, finally, solidified according to three different cooling conditions.

For the entire experimental campaign, the melting temperature was set at 800 ± 5 °C with 1 h holding time in order to guarantee the homogeneity of the molten bath and, potentially, the dissolution of any intermetallics. Periodically, the molten metal was gently skimmed.

The different cooling rates were achieved by varying the cooling conditions of the material while remaining inside the ceramic crucible. Pouring operations were deliberately avoided to limit any possible oxide entrapment that could promote the formation of Fe-rich particles [14].

More specifically, for the first and second batch of specimens, the crucible was removed from the furnace and cooled to room temperature (RT) by forced and still air (conditions *I* and *II*, respectively); for the third batch, the furnace was switched off and the material cooled by following the furnace inertia (condition *III*); the cooling conditions are summarized in Table 2.

Table 2. Cooling conditions used to cool down the experimental alloy from 800 °C to RT.

Cooling condition:	Method:
I	Forced air
II	Still air
III	Furnace inertia

The resultant as-cast specimens were longitudinally sectioned and prepared for microstructural investigations by standard metallographic procedures. The microstructural characterization was performed by using optical microscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and electron backscattered diffraction (EBSD).

The microstructural coarseness was estimated by measuring the secondary dendrite arm spacing (*SDAS*) which is strictly related the cooling rate [15]. EDS analysis was performed to evaluate the composition variations of the Fe-rich particles with respect to the morphology as well as the cooling conditions, while a combination of EDS and EBSD was performed to identify the phase and the crystallographic orientation of the compounds.

3. Results and discussion

3.1. Characterization of the HPDC alloy

Prior to investigating the evolution of the Fe-rich compounds as a function of the cooling rate, a microstructural characterization of base material produced by HPDC was also performed.

The microstructure of the diecast alloy is shown in Fig. 1. Due to the high cooling rate in the HPDC process, the alloy shows a refined microstructure with fine and fibrous eutectic Si particles, and the resultant *SDAS* value is about 10 μm. Coarse polyhedral and star-like particles with a mean diameter of ∼20 μm are uniformly distributed throughout the microstructure. Recently, it has been found that most of the polyhedral and star-like morphologies derive from a rhombic dodecahedron with, potentially, cavities on all the rhombic facets (Fig. 2) [16]. As the size of polyhedral and star-like compounds is comparable to the *SDAS* value, these compact particles are considered as pri-

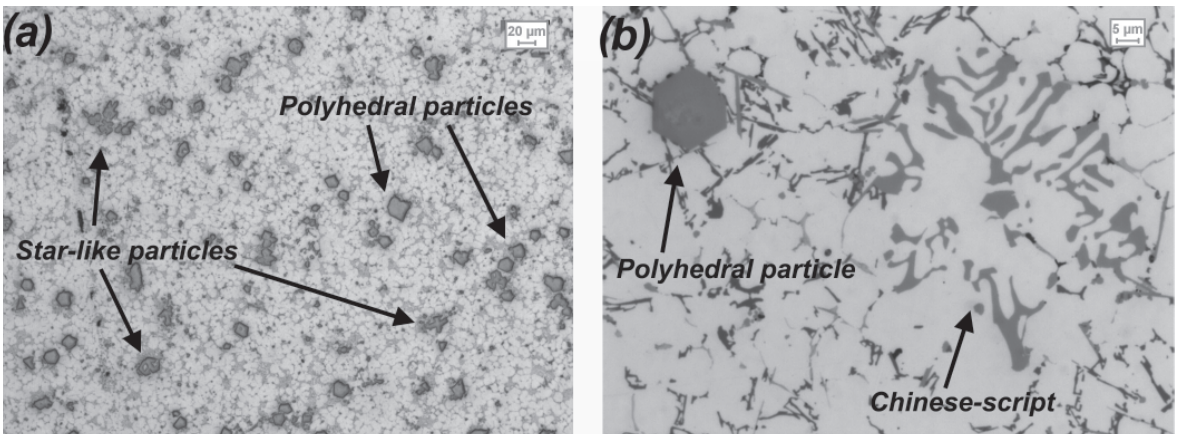

Fig. 1. Microstructure of HPDC specimens at (a) low and (b) higher magnifications; the Fe-rich compact (polyhedral and star-like) particles and the chinese-script structures are indicated.

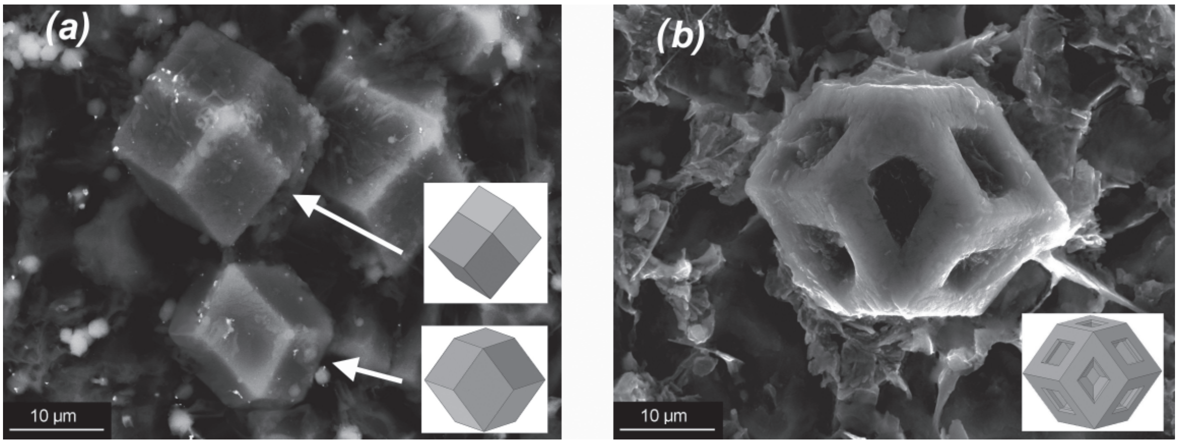

Fig. 2. 3-D SEM micrographs of a deep-etched HPDC sample showing α-Fe compact particles originated from (a) regular and (b) hollowed rhombic dodecahedron structure, as indicated in the insets [16].

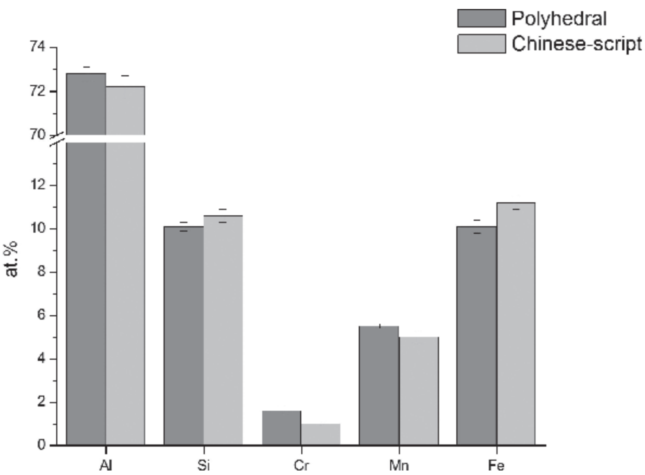

Fig. 3. Chemical compositions (at.%) of α-Fe particles as a function of their morphology (HPDC specimens).

mary phase and usually called *sludge*. In foundry processes, the tendency of sludge formation is strictly related to the Fe, Mn and Cr levels in the alloy as described by the following empirical formulation [17]:

$$\text{sludge factor } (SF) = 1 \times (\text{wt.\%Fe}) + 2 \times (\text{wt.\%Mn}) + 3 \times (\text{wt.\%Cr}) \quad (1)$$

According to Shabestari [18], the primary Fe-rich intermetallics precipitate for a sludge factor (*SF*) higher than 1.20, while the *SF* of the experimental alloy is 2.90, as indicated in Table 1. Besides compact particles, Fe-rich compounds with a chinese-script structure appear (Fig. 1b) and their branches seem to be well separated from the eutectic through α-Al phase grown at the boundary of the branches.

The EBSD investigations confirmed that the Fe-rich compact particles as well as the chinese-script structures are bcc α-Fe phase. Moreover, the same analysis revealed that the chinese-script morphology consists of a single interconnected structure; this result seems to be in agreement with the SEM observations of deep-etched samples [15, 19–21].

The chemical composition of the α-Fe phase was studied as a function of morphology using EDS and the results are reported in Fig. 3. The primary compact particles show lower Si content and a lower Fe : (Mn + Cr) ratio than the chinese-script compounds; however, due to the mutual replacement of Fe, Mn and Cr atoms, the stoichiometry of the compact and chinese-script structures can be considered almost equal and consistent with both α-$Al_{12}(Fe,Mn,Cr)_3Si_2$ and $Al_{15}(Fe,Mn)_3Si_2$ phases. Concerning the chemical variations as a function of morphology, similar results are also reported by Warmuzek et al. [22] who found that, during solidification of a hypoeutectic Al–Si alloy, primary α-Fe particles precipitate with polyhedral shape and relatively higher Mn content than secondary α-Fe chinese-script structures.

3.2. Influence of cooling rate

The microstructures resulting from the three different solidification conditions are reported in Fig. 4. Upon decreasing the cooling rate, the microstructure became coarser. The microstructural scale of the as-cast samples was estimated using *SDAS* values: the mean values are approximately 25, 40 and 110 µm for the conditions *I*, *II* and *III*, respectively.

Coarse chinese-script Fe-rich compounds increase in size as the cooling rate decreases and seem to assume a more skeleton-like morphology (Fig. 5a). This outcome is in agreement with Verma et al. [7], who found that the size and the secondary dendrite arm spacing of the α-Fe chinese-script intermetallics increase with decreasing cooling rate.

Additionally, coarse Fe-rich dendrites form under solidification conditions *I* and *II*, while Fe-rich dendrites are completely substituted by coarse needle-like compounds as the cooling rate is further reduced (condition *III*). Under such cooling conditions, coarse blocky particles have the time to settle at the bottom of the sample (Fig. 5b). At very slow solidification, primary blocky Fe-rich particles tend to sediment due to higher density.

It is well known how the formation of primary Fe-bearing compounds depends on the alloy's chemistry as well as on the holding temperature and time. Dunn [23], Gobrecht [24] and Jorstad [17] found an empirical relationship for Al–Si–Cu alloys between the sludge factor and the critical precipitation temperature below which Fe-rich particles tend to form in the holding furnace. According to the Shabestari's results [18], the temperature of sludge formation depends especially on the initial Fe content following this relationship:

$$\text{Temperature}\,(^\circ\text{C}) = 645.7 + 34.2 \times (\text{wt.\%Fe})^2 \qquad (2)$$

In the present work, the holding temperature (i.e. 800 °C) was enough to avoid sludge formation and modification inside the ceramic crucible. Therefore, the nucleation and growth mechanisms are mainly controlled by the changing cooling rate.

According to the chemical compositions established from the EDS analysis, the chinese-script particles, the coarse dendrites and blocky compounds can be associated to α-Fe phase, while the large needle-like particles are consistent with β-Fe. The EBSD phase map confirms the crystal structure of α-Fe phase (bcc with lattice parameter: $a \sim 1.26$ nm) for the chinese-script particles (Fig. 6a). As

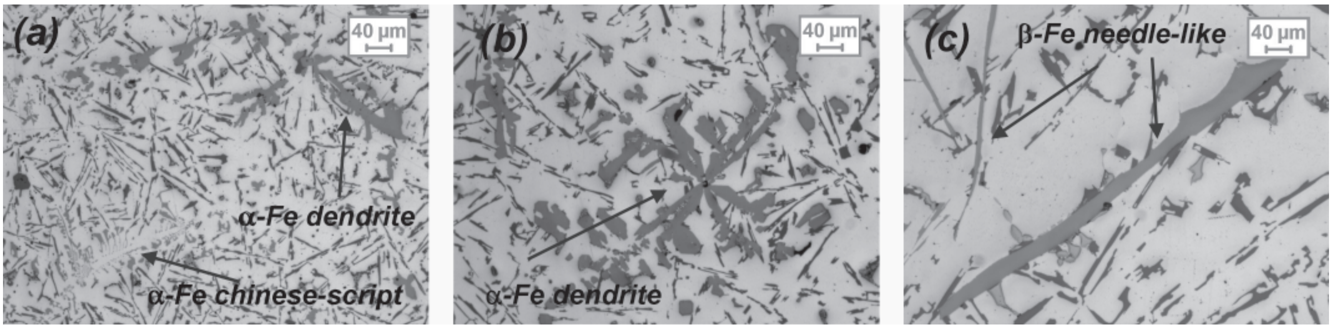

Fig. 4. Microstructures of the experimental alloy obtained under the following solidification conditions: (a) *I*, (b) *II* and (c) *III*.

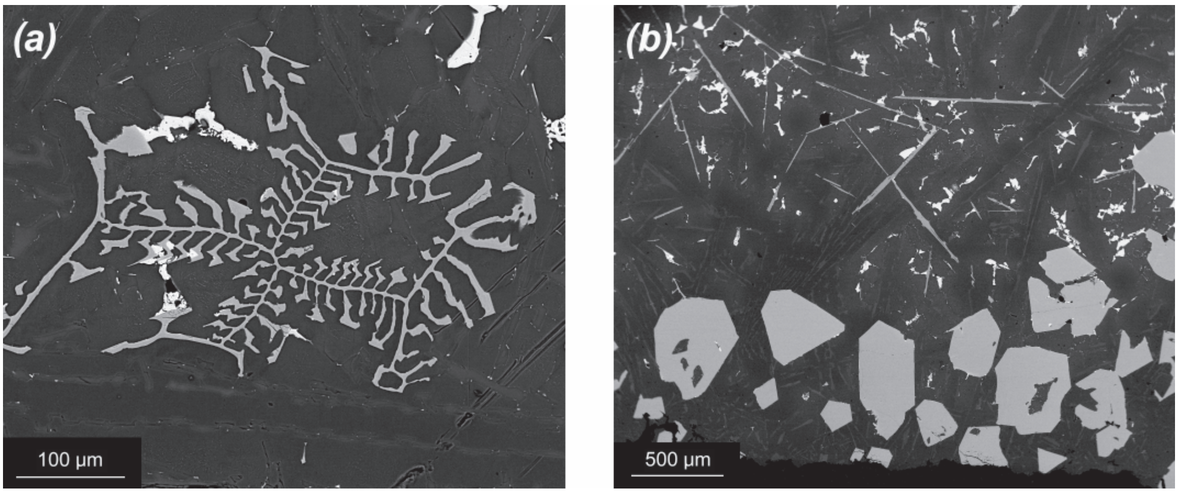

Fig. 5. SEM micrographs of (a) coarse α-Fe chinese-script compound in the alloy cooled according condition *II* and (b) large α-Fe blocky particles settled at the bottom of the sample cooled under condition *III*.

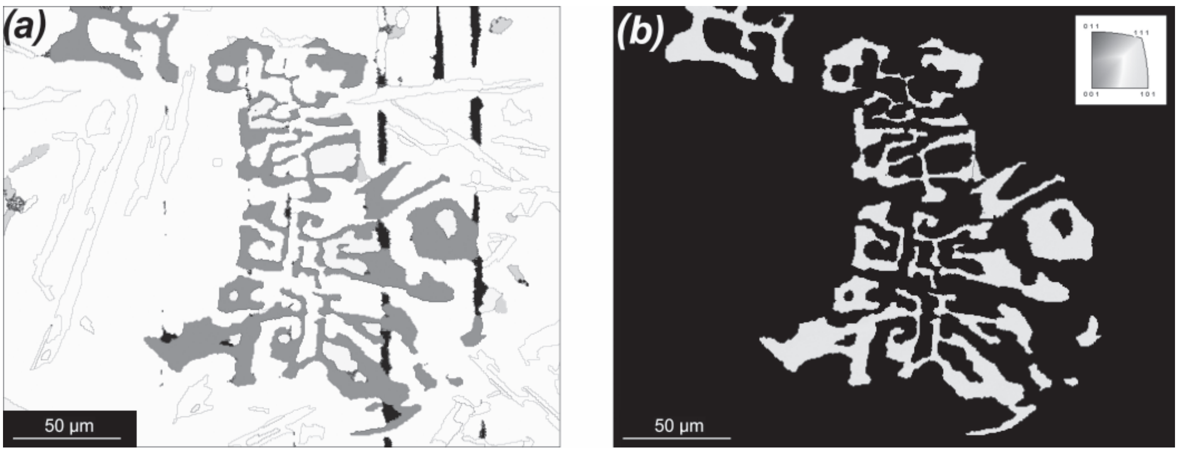

Fig. 6. (a) EBSD phase map (white = α-Al and Si; dark grey = α-Fe; light grey = Al_2Cu; black = no indexed points) and (b) corresponding orientation map of the α-Fe chinese-script in the sample cooled under condition *I*.

shown in the orientation map in Fig. 6b, all the single branches of the chinese-script structure show the same crystallographic orientation, confirming the interconnected nature of such a branched structure.

The EDS showed that the chemical composition of the α-Fe phase is sensitive to morphology, as already found for the HPDC specimens. The chinese-script structures show a relative higher Fe content (or equivalently higher Fe : (Mn + Cr) ratio) and higher Cu level than the dendrites and coarse blocky particles (Fig. 7). The presence of Cu in the α-Fe phase has been already reported in Refs. [3, 10]; Belmares-Perales et al. [12] suggested a stoichiometry close to $(Al,Cu)_{12}(Fe,Cr,Mn)_3Si_2$ for Cu bearing α-Fe compounds. However, the present authors also agree with the $Al_{12}(Fe,Cr,Mn,Cu)_3Si_2$ stoichiometry for Cu-enriched chinese-script structures because Cu, being a transition element along with Cr and Mn, could replace some Fe atoms in the cubic lattice of the phase.

By taking into account the EDS results, it is possible to affirm that generally the chinese-scripts compounds present

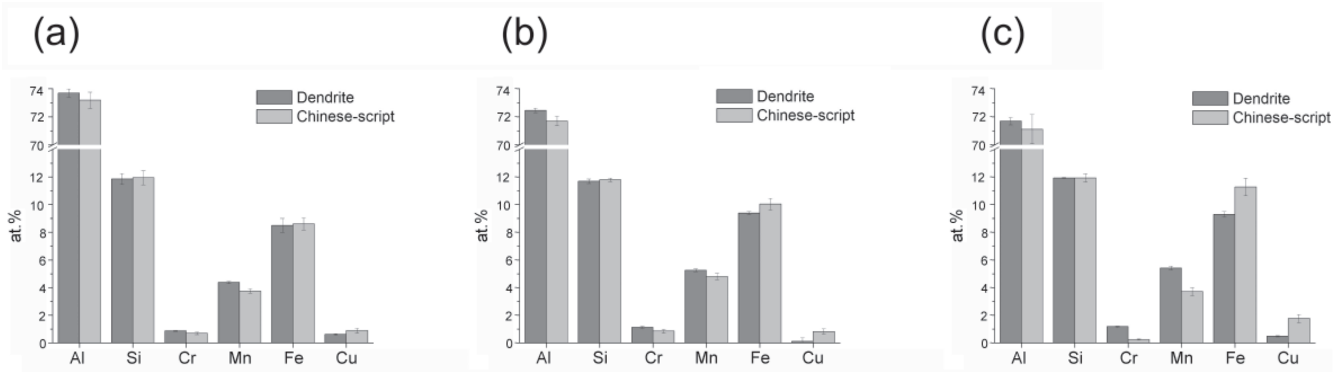

Fig. 7. Chemical compositions (at.%) of α-Fe phase as functions of the different morphologies achieved under the following solidification conditions: (a) *I*, (b) *II* and (c) *III*.

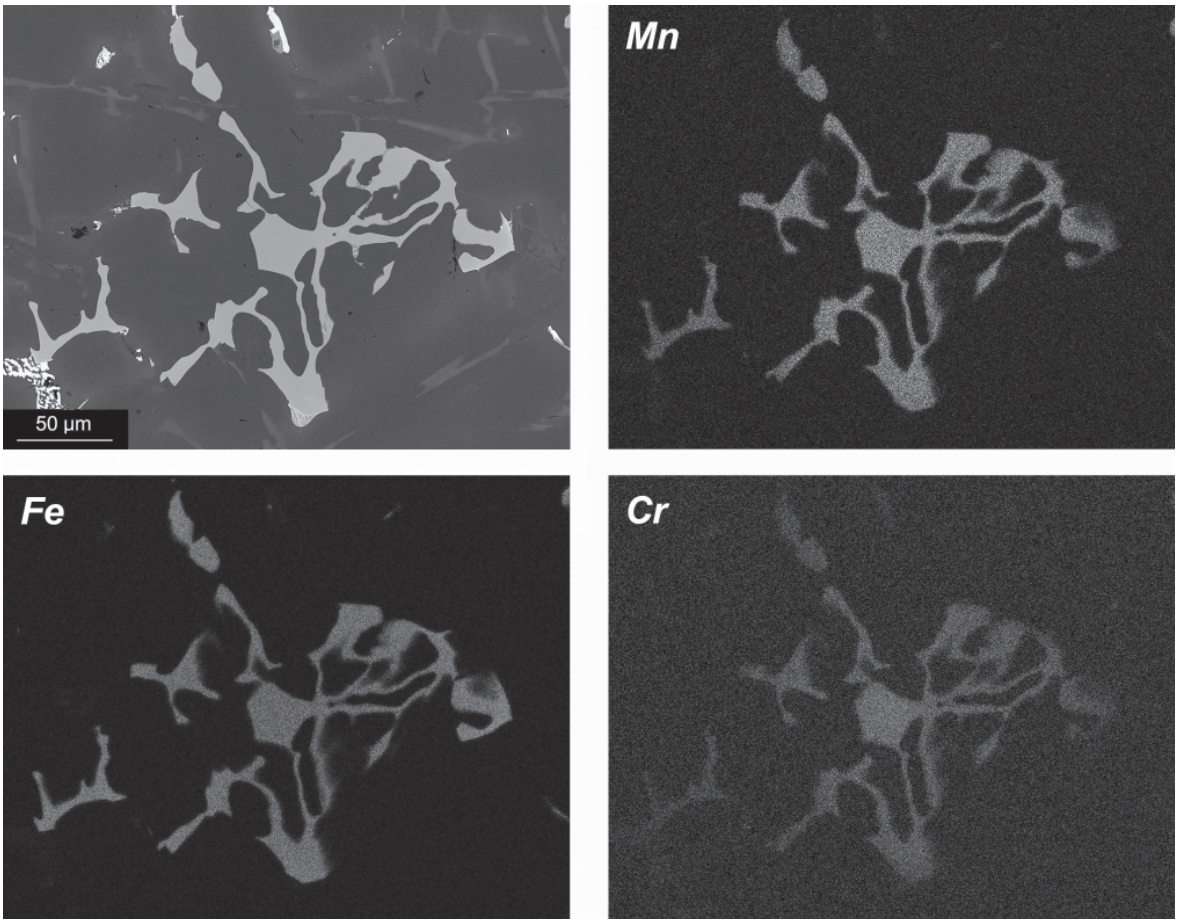

Fig. 8. SEM micrograph of a branched α-Fe structure with the associated Cr, Fe and Mn EDS maps.

a relatively lower (Mn + Cr) content than coarse blocky particles and coarse dendrites. The Cr and Mn distribution maps of a chinese-script structure appearing in the sample under the solidification condition *I* seem to verify such an outcome (Fig. 8): it appears that the concentration of Mn and Cr decreases by moving from the blocky particle in the centre of the structure toward the peripheral branches.

4. Conclusions

The evolution of morphology and chemical composition of α-Fe phase in a secondary Al–Si–Cu alloy has been investigated as a function of the cooling rate. The following conclusions can be drawn from this work.

- By reducing the cooling rate, the microstructural scale generally increases: the chinese-scripts enlarge by assuming a more skeleton-like morphology and coarse α-Fe dendrites grow.
- At lower cooling rate, the α-Fe dendrites completely disappear and large platelet-like and needle-like β-Fe particles settle, as well as coarse α-Fe blocky compounds, at the bottom of the sample.
- The chinese-script compounds are α-Fe single interconnected structures, as confirmed by EBSD analysis, and the EDS results show that such branched structures have higher Fe : (Mn + Cr) ratio than the sludge and coarse blocky particles as well as coarse dendrites.

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Correspondence address

Dr. Alberto Fabrizi
Department of Management and Engineering
University of Padua
Stradella San Nicola, 3
36100 Vicenza
Italy
Tel.: +39 339 199 62 60
E-mail: fabrizi@gest.unipd.it

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