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Manufacturing of Al-Zr-Si master alloy from zircon concentrate

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Abstract. Aluminum alloy of thermal-resistant aluminum alloy wire for overhead line conductors usually contains zirconium, silicon, iron, and other components. Hence, Al-Zr-Si master alloy can be used to produce thermal-resistant aluminum alloy. In this study, the manufacturing procedure of Al-Zr-Si master alloy from zircon concentrate has been introduced. The zircon concentrate was thoroughly mixed with different amounts of KCl and Na_2SiF_6 or Na_3AlF_6, then sintered in an electric muffle furnace at 700 ^oC for 2 hrs with automatic temperature control. The sinter was premixed with Na_3AlF_6 at the 1:1 ratio and dried at 140-160^{o}C to remove the humidity. The powder mixture was added to the aluminum molten at 1200^{o-}C and then stirred well to ensure proper powder mixing in the melt. After the finish reaction and slag skimming, the melt was taken out of the furnace and poured into the mold. The master alloy was characterized by a spectrometer, ICP-OES, and optical microscopy.

Keywords: Al-Zr-Si master alloy, thermal-resistant aluminum alloy, zircon concentrate

Classification numbers: 2.9.1, 2.10.2

1. INTRODUCTION

Aluminum alloy of thermal-resistant aluminum alloy wire for overhead line conductors usually contains zirconium, silicon, iron, and other components. For example, aluminium alloys contain, (wt. %): zirconium 0.2 - 0.32, iron 0.15 - 0.42, silicon 0.02 - 0.1 [1]; zirconium 0.1 - 0.19, iron 0.21 - 0.35, silicon 0.11 - 0.15 [2]; etc.

A transition metal as Zr is used to improve the strength at room temperature and to provide the retention of the structure and tensile properties at elevated temperatures due to the formation of Al_3Zr dispersoids during homogenizing treatment [3] The choice of Si as an alloying element was due to its effect on the kinetics of nucleation of secondary particles. Si is capable of accelerating the nucleation of the secondary particles in aluminum alloys of Al–Zr. Therefore, Si accelerates the decomposition of the solid solution for alloys of Al-Zr [4]. It is shown that even at low concentrations silicon fractions (0.25 wt.%) can be expected to accelerate the decomposition of aluminum solid solution (Al) for zirconium, as well as phase fragmentation of Al_8Fe_2Si during heat treatment, which significantly affects the resistivity already at a temperature stepwise annealing at 400 °C [5]. Iron allows to achieve additional strengthening due to the formation of crystal phase Al_3Fe in the structure [6]. It is also known that, at a certain ratio of elements (Si:Fe = 0.3 - 0.5), a decrease in the resistivity can be achieved while maintaining the effect of hardening due to the formation of the pleasant morphology in the phase composition [5, 6].

For melting these thermal-resistant aluminum alloys, it is necessary to produce master alloys of Al-Si, Al-Zr, etc. However, the melting of Al-Zr and Al-Si master alloys often requires expensive raw materials.

Al-Si master alloy contains 12 - 15 % silicon and the rest is aluminum. When preparing Al-Si master alloy, aluminum is first melted and heated to 850 - 900 ^{o}C. Silicon heated to 100 - 200 °C is introduced in small portions (in the form of pieces, 20 - 30 mm in size) into molten aluminum under cover flux. In order to accelerate the dissolution of silicon, it is constantly immersed in a liquid melt using a graphite stirrer. At the end of the dissolution of the last silicon additive, the alloy is thoroughly stirred and poured into molds at a temperature of 700 - 720 °C [7].

The method of direct alloying of aluminum and pure zirconium is used extremely rarely. The process is preferably carried out in induction furnaces. Zirconium powder with granulated aluminum grains in the form of pressed briquettes is introduced into liquid aluminum superheated to a temperature of 1200 - 1300 °C. The melt is thoroughly mixed until each portion is completely dissolved. After the complete dissolution of zirconium at a temperature of 950-1000 °C, the melt is refined with $MnCl_2$ salt and poured [8].

The disadvantages of direct melting methods is the use of relatively expensive starting materials in a metal form, a large loss of metals during melting.

A method is proposed for obtaining an aluminum-zirconium master alloy by introducing potassium fluorozirconate K_2ZrF_6 in two steps: primary aluminum is overheated to 1100-1200 °C. Salt is thrown onto the surface of the melt and stired into the melt; before the second addition of salt, the melt is again overheated to 1200 °C [8]. However, this method uses expensive potassium fluorozirconate. The complete extraction of zirconium into the alloy is not achieved and, as a result, significant losses of zirconium with slag occur. In addition, there is an increased gas emission and, accordingly, pollution of the atmosphere from the smelting and foundry stages with fluorine compounds.

There are also other methods for producing aluminum-zirconium master alloys, for example, using zirconium tetrachloride and zircon concentrate as zirconium-containing raw materials.

When obtaining aluminum-zirconium master alloys from zirconium tetrachloride, first, the initial mixture of chlorides is melted in a crucible, containing 35 - 40 % zirconium tetrachloride and 50 - 65 % sodium and potassium chlorides (an equimolar ratio of sodium and potassium chlorides is optimal). Then, pieces or molten aluminum in an amount approximately four times higher than that necessary for the reduction of zirconium are introduced into the salt melt, and heated to 700 - 750 ºC. After thorough mixing, the melts of the crucible are allowed to settle, the salt melt is drained from the molten slag-alloy.

The method of production of aluminum-zirconium alloys using zircon concentrate as a zirconium-containing material is characterized by a higher process temperature – 1000 - 1100 ºC. Zircon concentrate is introduced into aluminum in portions (with thorough mixing) under a layer of cryolite. Cryolite consumption is 6 - 8 % by weight of the charge, and concentrate – 20 - 24 % by weight of aluminum.

According to the decision approving the zoning plan for exploration, extraction, processing and exploitation of titan ores by 2020 with vision to 2030 of the Prime Minister of Viet Nam, Viet Nam's titanium ore deposits and resources are estimated at around 650 million tons of heavy minerals (including about 78 million tons of zircon) [9]. However, the products of titanium enterprises are only in the form of concentrates containing titanium, zircon, and monazite for export. Only a few enterprises have invested in facilities to grind zircon powder and reduce ilmenite to smelt titanium slag.

Therefore, this research aims to study the manufacturing of Al-Zr-Si master alloys from relatively cheap zircon concentrate and create valuable products from zircon concentrate.

2. MATERIALS AND METHODS

2.1. Materials

Al-Zr-Si master alloy was prepared using commercial pure aluminum and zircon concentrates produced by Binh Dinh Minerals Joint Stock Company. Chemical compositions of the raw materials are given in Table 1 and Table 2.

Table 1. Chemical composition of aluminum.

Aluminum grade	Composition, %						
	Al	Zr	Fe	Si	Cu	Zn	Ti
Pure Al	99.8	0.01	0.10	0.04	0.01	0.01	0.01

Table 2. Chemical composition of zircon concentrate.

Zircon concentrate	Composition, %			
	ZrO_2	SiO_2	TiO_2	Fe_2O_3
Zirconium silicate	64.8	32.3	0.06	0.15

Cryolite Na_3AlF_6 (≥ 99.0 %), sodium silicofluoride Na_2SiF_6 (≥ 99.0 %), sodium chloride NaCl (≥ 99.5 %), and potassium chloride KCl (≥ 99.5 %) were used for the sintering of zircon concentrate and preparation of flux in the smelting of Al-Zr-Si master alloy.

2.2. Methods

The beginning of Al-Zr-Si master alloy melting was to sinter the zircon concentrates with potassium chloride and sodium silicofluoride or with potassium chloride and cryolite. When carrying out the sintering process, a portion of zircon concentrate was thoroughly mixed with the potassium chloride and sodium silicofluoride or with the potassium chloride and cryolite in a corundum crucible. The sintering was carried out in an electric muffle furnace at 700 °C for 2 hours with automatic temperature control. After cooling, the sintered material was finely grounded

The material proportions for sintering zircon concentrate are given in Table 3.

Al-Zr-Si master alloys were prepared by three different experimental modes. The first experimental mode involved the addition of zircon concentrate into molten aluminium without sintering. In the second experimental mode, zircon concentrate was replaced with a finely ground sinter of zircon concentrate, Na_2SiF_6, and KCl. In the third experimental mode, the ground sinter of zircon concentrate, Na_2SiF_6, and KCl was replaced with the ground sinter of zircon concentrate, Na_3AlF_6, and KCl.

Pieces cut from aluminum ingots were first loaded in the graphite crucible in an electric resistance furnace and heated to 1100-1200 °C under a cryolite flux cover. Cryolite cover flux was taken in an amount of 6 - 8 % by weight of the charge. Zircon concentrate or ground sinters were premixed with cryolite in a ratio of 1:1 and dried at 140 - 160 °C to remove the humidity, then added to the melt in certain portions. The melt was stirred well with a titanium rod to ensure proper mixing of powder in the melt. After introducing the last portion of the powder mixture, the melt was heated to 1000 °C. Then the slag was skimmed out. The melt was poured into the mould. Table 3 shows the details of conditions for the preparation of Al-Zr-Si master alloys.

Table 3. Al-Zr-Si master alloys prepared under different conditions.

Master alloy No	Aluminum ingot (g)	Material proportions for zircon concentrate sintering					Meting temperature (°C)
		Zircon concentrate (g)	KCl (g)	Na_2SiF_6 (g)	Na_3AlF_6	Mole ratio of $ZrSO_4$:KCl: Na_2SiF_6 or Na_3AlF_6	
First experimental mode							
1	1120	117	-	-	-	-	1100
2	1060	310	-	-	-	-	1200
Second experimental mode							
3	1000	100	81	103	-	1:2:1	1200
4	1000	100	102	128	-	1:2.5:1.25	1200
5	1000	100	122	154		1:3:1.5	1200
Third experimental mode							
6	1000	100	122	-	115	1:3:1	1200
7	1000	100	153	-	143	1:3.8:1.28	1200
8	1000	100	183	-	172	1:4.6:1.5	1200
9	1000	100	214	-	200	1:5.4:1.8	1200

The composition of Al-Zr-Si master alloys was analyzed by an optical emission spectrometer (SPECTROLAB LAVM12) and inductively coupled plasma-optical emission spectrometers (PerkinElmer Avio 500 ICP Optical Emission Spectrometer and PerkinElmer Optima 5300 DV ICP-OES Spectrometer).

Standard metallographic techniques were used to prepare the sample for microstructural analysis. These prepared samples were etched using 3 % HF in water to study the microstructure under the optical microscope (OLYMPUS MPE3).

3. RESULTS AND DISCUSSION

The chemical composition of melted Al-Zr-Si master alloys is given in Table 4. In the first experimental mode, zircon and silicon contents of Al-Zr-Si master alloys are low because ZrO_2 is a difficult oxide to reduce. The Gibbs energy change of reaction $ZrO_2 + 4/3Al = Zr + 2/3Al_2O_3$ at a temperature of 1100-1200 ^oC has a positive value [10]. Furthermore, ZrO_2 and SiO_2 are in the $ZrSiO_4$ compound (zircon), so their reduction is more difficult.

In the second experimental mode, zircon and silicon contents of Al-Zr-Si master alloys are higher since the following reactions may occur in the sintering stage:

$$Na_2SiF_6 + 2KCl = K_2SiF_6 + 2NaCl \quad (1)$$

$$K_2SiF_6 + ZrSiO_4 = K_2ZrF_6 + 2SiO_2 \quad (2)$$

$$Na_2SiF_6 + 2KCl + ZrSiO_4 = K_2ZrF_6 + 2NaCl + 2SiO_2 \quad (3)$$

[11]

with high probability, the mechanism of reaction (2) is as follows [12]:

$$K_2SiF_6 \rightleftarrows SiF_4 + 2KF \quad (4)$$

$$ZrSiO_4 + SiF_4 \rightleftarrows ZrF_4 + 2SiO_2 \quad (5)$$

$$ZrF_4 + 2KF \rightleftarrows K_2ZrF_6 \quad (6)$$

Sintering was carried out at 700 °C because at 650 - 700 ^oC, 97 - 98 % of zircon decomposes. At temperatures above 700 ^oC, K_2SiF_6 quickly dissociates, and part of SiF_4 evaporates with gases, not having time to react with zircon. There is also a possibility of zircon loss due to the evaporation of ZrF_4. At 713.3 ^oC, the vapor pressure of ZrF_4 is 7.24 mmHg [12].

In the melting stage, K_2ZrF_6 and SiO_2 were reduced by reactions [7, 8]:

$$3K_2ZrF_6 + 4Al = 6KF + 4AlF_3 + 3Zr \quad (7)$$

$$3SiO_2 + 4Al = 3Si + 2Al_2O_3 \quad (8)$$

When sintering zircon concentrate to melt Al-Zr-Si master alloy No. 3, the mole ratio of the materials was selected according to the stoichiometric ratio of reaction (3). When sintering zircon concentrate to smelt Al-Zr-Si master alloys No. 4, and No. 5, the amount of KCl and Na_2SiF_6 increased by 25 % and 50 %, respectively, compared to the stoichiometric ratio.

Table 4 and Figure 1 show that when increasing the amount of KCl and Na_2SiF_6 in the sintered material mixture by more than 25 % and 50 % compared to the stoichiometry, the content of Zr and Si in the master alloy increases. Since during the sintering process, K_2SiF_6 decomposes to form volatile SiF_4, it is necessary to increase its concentration to compensate for this evaporation. As the amount of K_2SiF_6 increases, the amount of KCl and Na_2SiF_6 also increases according to the stoichiometric ratio of reaction (1). Furthermore, increasing the amount of KCl will inhibit the dissociation of K_2SiF_6 [12]. However, in these master alloys, the content of Zr is about equal to the Si content. Such master alloys are not suitable for producing thermal-resistant aluminum alloy wire because aluminum ingots always contain some amount of Si, so they will increase the Si content too high. These master alloys can be used to add zirconium to Al-Si casting alloys for grain refinement [13], to type 354 Al-Si-Cu-Mg casting alloys for enhancing ambient- and elevated-temperature tensile properties, hardness, and impact properties [14], or used to melt aluminum alloy containing Si and Zr, such as alloy 6205 (0.8 % Si, 0.5% Mg, 0.1% Mn, 0.1% Cr, and 0.1% Zr), etc.

Table 4. Chemical composition (by wt.%) of Al-Zr-Si master alloys.

Master alloy No	Chemical composition (by wt.%)						
	Zr	Fe	Si	Cu	Mn	Mg	Zn
First experimental mode							
1	0.1365	0.1040	0.2130	0.0040	0.0010	0.0030	0.0010
2	0.2246	0.1080	0.3800	0.0040	0.0010	0.0050	0.0030
Second experimental mode							
3	2.2600	0.4810	2.1720	0.0080	0.0040	0.0040	0.045
4	2.4100	1.5970	2.3710	0.0110	0.0060	0.0040	0.0100
5	3.1400	0.2570	3.1080	0.0060	0.0030	0.0080	0.0000
Third experimental mode							
6	2.0300	0.2240	1.1510	0.0060	0.0030	0.0040	0.0170
7	2.2700	1.2050	1.0680	0.0060	0.0050	0.0040	0.0050
8	2.6200	1.2150	1.9110	0.0060	0.0050	0.0030	0.0050
9	2.0200	0.2820	2.3890	0.0050	0.0040	0.0050	0.0300

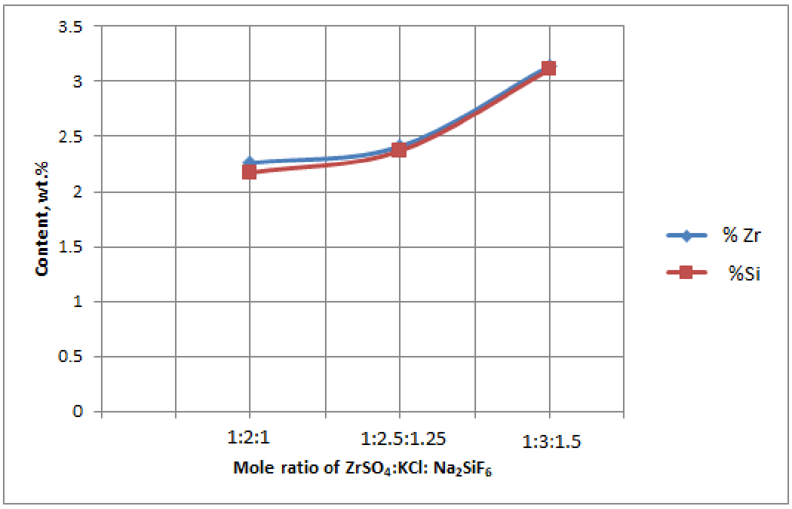


Figure 1. Effect of mole ratio of $ZrSO_4$:KCl: Na_2SiF_6 on the content of Zr and Si in Al-Zr-Si master alloys.

In the third experimental mode, zircon and silicon contents of Al-Zr-Si master alloys are also higher than their content in the first experimental mode. In the sintering stage of the third experimental mode, the following reactions may occur [15]:

$$4Na_3AlF_6 + 12KCl = 4K_3AlF_6 + 12NaCl \quad (9)$$

$$4K_3AlF_6 = 12KF + 4AlF_3 \quad (10)$$

$$ZrO_2 + 6KF = K_2ZrF_6 + 2K_2O \quad (11)$$

$$3ZrO_2 + 6KF + 4AlF_3 = 3K_2ZrF_6 + 2Al_2O_3 \quad (12)$$

$$4ZrO_2 + 4Na_3AlF_6 + 12KCl = 4K_2ZrF_6 + 12NaCl + 2K_2O + 2Al_2O_3 \quad (13)$$

or $2Na_3AlF_6 + 6KCl + 2ZrO_2 = 2K_2ZrF_6 + 6NaCl + K_2O + Al_2O_3$ (14)

When sintering zircon concentrate to smelt Al-Zr-Si master alloy No. 6, the mole ratio of the materials was selected according to the stoichiometric ratio of reaction (14). When sintering zircon concentrate to smelt Al-Zr-Si master alloys No. 7, No. 8, and No. 9, the amount of KCl and Na_3AlF_6 was increased by 25 %, 50 %, and 75 %, respectively, compared to the stoichiometric ratio.

Table 4 and Figure 2 show that when increasing the amount of KCl and Na_3AlF_6 in the sintered material mixture by more than 25 % and 50 % compared to the stoichiometry, the content of Zr and Si in the master alloy increases. Since during the sintering and melting processes, K_2ZrF_6 decomposes to form volatile ZrF_4, it is necessary to increase its concentration to compensate for this evaporation. When the amount of K_2ZrF_6 increases, the amount of KCl and Na_3AlF_6 also increases according to the stoichiometric ratio of reaction (14). However, if the amount of KCl and Na_3AlF_6 is further increased by more than 75 % compared to the stoichiometry, the content of Si continues to increase but the content of Zr decreases. One reason for this is that the increased content of KCl and Na_3AlF_6 in the sintering mixture may increase the melting temperature of the sintering phases, thus reducing the recovery of K_2ZrF_6 in the sinter.

In the melting stage, K_2ZrF_6 and SiO_2 were reduced by aluminum to form Zr and Si according to reactions (7), and (8).

Alloys No.6, No.7, and No.8 have higher Zr content than Si content, therefore they are suitable for producing thermal-resistant aluminum alloys.

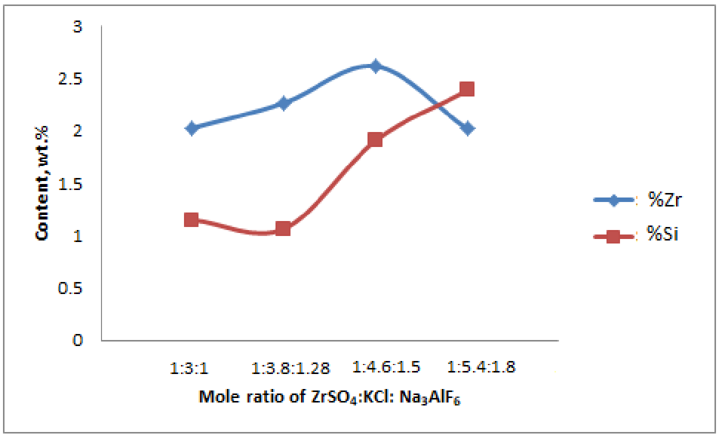
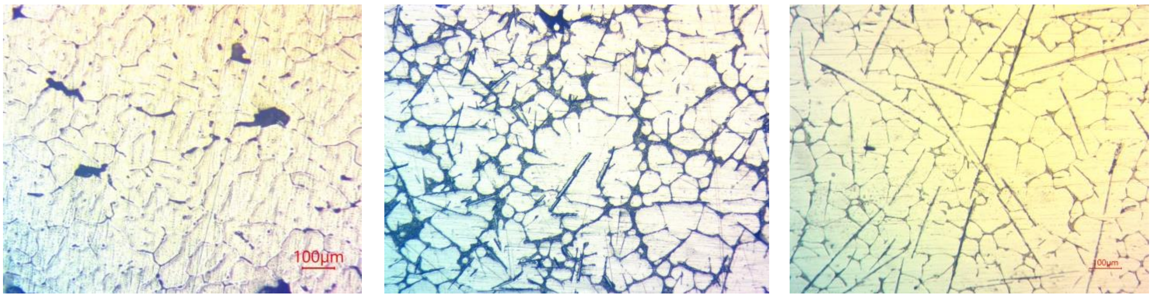


Figure 2. Effect of mole ratio of $ZrSO_4$:KCl: Na_3AlF_6 on the content of Zr and Si in Al-Zr-Si master alloys.

Figures 3a, 3b, and 3c show microstructures of Al-Zr-Si master alloys No.2, No.5, and No.6. As shown in Figure 3a, in the microstructure of master alloy No.2, there is almost only α solid solution phase. Because the Si and Zr contents are too small, the Si and $ZrAl_3$ phases are invisible. Alloy No.5 has a relatively high content of Si and Zr, so the $ZrAl_3$ needle-shaped and (α-Si) eutectic phases appear clearly in the microstructure (Figure 3b). In the microstructure of master alloy No.6 (Figure 3c), there are also $ZrAl_3$ and (α-Si) eutectic phases. However, because the Si content is less than the Zr content, the amount of ZrAl3 phase is dominant.



a) b) c)

Figure 3. Microstructure of Al-Zr-Si master alloys (x50): a) Master alloy No.2, b) Master alloy No.5, c) Master alloy No.6.

According to the isothermal section diagram of the Al-Zr-Si system at 900 ^{o}C [16], the liquidus temperatures of the prepared Al-Zr-Si master alloys, which contain 2.020-3.140 % Zr and 1.068-3.108 % Si, are below 900 ^{o}C, whereas those of Al-Zr master alloys containing 2-4 % Zr are 950-1050 ^{o}C [8]. Therefore, Al-Zr-Si master alloys can be added to aluminum melt for alloying or grain refinement at temperatures lower than those for the added Al-Zr master alloys.

However, the manufacturing of Al-Zr-Si master alloys from zircon concentrates by the above modes may produce atmospheric emissions consisting of particulate fluorides: Na_3AlF_6, K_3AlF_6, Na_2SiF_6, K_2SiF_6, K_2ZrF_6, KF, AlF_3; gaseous fluorides: SiF_4, ZrF_4; particulate chlorides: KCl, NaCl; particulate zircon, and silicon oxide; etc. In the case of the inhalation of dust and gases, the effect on the respiratory tract is significant. Chlorides and fluorides have a corrosive and irritant effect on the skin, eyes, mouth, esophagus, and stomach. The toxic effect is caused by the evolution of hydrochloric and hydrofluoric acids when chlorides and fluorides are exposed to moist air. To control atmospheric emissions, the evolved dust and gases need to be collected, which are then ducted to pollution control equipment [17].

4. CONCLUSIONS

Al-Zr-Si master alloys have been successfully manufactured by reaction of aluminum with the sinter of zircon concentrate, Na_2SiF_6, KCl, and with the sinter of zircon concentrate, Na_3AlF_6, KCl.

The Al-Zr-Si master alloys were manufactured from the sinter of zircon concentrate, Na_2SiF_6, and KCl, which have a Zr content of about 2.26-3.14% and a Si content of about 2.172 - 3.108 %. However, in these master alloys, the content of Zr is about equal to the content of Si. These master alloys are not suitable for producing thermal-resistant aluminum alloy wire. They can be used to melt other aluminum alloys containing Zr and Si or grain-refined aluminum alloys containing Si.

The Al-Zr-Si master alloys were manufactured from the sinter of zircon concentrate, Na_3AlF_6, and KCl, which have a Zr content of about 2.02 - 2.62 % and a Si content of about 1.151 - 2.389 %. Master alloys No.6, No.7, and No.8 were manufactured with the amount of KCl and Na_3AlF_6 in the sintered material mixture according to the stoichiometric ratio and 25 %, 50 % more than the stoichiometry. These master alloys have lower Si content than Zr content, therefore suitable for producing thermal-resistant aluminum alloys.

The third experimental mode, with the amount of KCl and Na_3AlF_6 in the sintered material mixture greater than 50 % compared to the stoichiometry, represents the best manufacturing condition for Al-Zr-Si master alloys to melt thermal-resistant aluminum alloys.

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Declaration of competing interest. The authors confirm that they have no competing interest in publishing the article.

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