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Microstructure, billet surface quality and tensile property of $(Al_2O_3+Al_3Zr)_p/Al$ composites in situ synthesized with electromagnetic field

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A B S T R A C T

The aluminum matrix composites reinforced by Al_2O_3 and Al_3Zr particulates were fabricated via in situ chemical reaction between Al–15 wt.% $Zr(CO_3)_2$ systems. In the process of in situ reaction, a low frequency electromagnetic field (EMF) is employed to improve the conditions of reaction between reactants powder and melt. The optimized electromagnetic density of low frequency EMF is 0.025 T. During the direct chill casting process of composites melt, the custom-designed electromagnetic fields are introduced to control the microstructures and improve the billet surface quality. XRD analysis shows that Al_2O_3 and Al_3Zr reinforcement phases have been obtained. The Lorenz force improves the kinetic condition and accelerates the nucleation of endogenetic particulates. Microstructure analysis by SEM indicates that the average size of particulates and grain size of matrix are refined to 0.5–1 μm and 20–40 μm, respectively. The surface quality of round billet is greatly improved by the high frequency EMF. The results of tensile properties test show that the tensile strength of composites in situ fabricated with EMF is 254.6 MPa, which is increased by about 104 MPa and 69.4% compared with those of composites in situ fabricated without EMF.

1. Introduction

In recent years, with the increasing demands for high-performance structural materials particle reinforced aluminum matrix composites (PRAMCs) have attracted a lot of attention due to their excellent performances, such as light density, high specific stiffness, high specific strength and good thermal stability compared with pure aluminum and their alloys [1,2]. The PRAMCs can be fabricated by ex situ synthesis and in situ synthesis [3,4]. In ex situ methods, the particulates, which are prepared separately prior to the composites fabrication, are added into the metal during fabrication process. There are some defects and difficulties to fabricate composites by ex situ methods. For example, the interfacial reactions are likely to occur between the reinforcement and the matrix during fabrication process. Furthermore, the particle sizes are difficult to be controlled and the distribution of fine particulates is comparatively non-uniform. These defects take a deadly effect on material properties. In in situ process, the reinforcement phases are formed in the metallic matrix by in situ chemical reaction during composites fabrication process. There are many advantages for PRAMCs fabricated by in situ method. For example, the in situ formed reinforcement phases are thermodynamically stable, free of surface contamination and disperse more uniformly in the matrix, leading to stronger particle–matrix bonding. These outstanding features make in situ PRAMCs posses excellent mechanical properties. Now, a variety of processing techniques have been developed to fabricate PRAMCs by in situ process, such as direct melt reaction technique (DMR), reactive hot pressing (RHP), self-propagating high temperature synthesis (SHS), and so on [5].

Our previous studies on PRAMCs have shown that Al_3Zr and Al_2O_3 can be formed in situ by means of DMR process. The Al_3Zr and Al_2O_3 particulates reinforced aluminum matrix composites exhibit high hardness, superior wear resistance, high melting point, good thermal stability, high stiffness and high strength at elevated temperature. However, the microstructure of composites especially the particulates dispersion needs to be improved. Some external fields such as electromagnetic field, ultrasonic field and electric field are introduced in the synthetic process of PRAMCs in order to improve the materials microstructure and properties [6,7].

In this paper, $Al–ZrO_2(Zr(CO_3)_2)$ components are utilized to synthesize $(Al_2O_3+Al_3Zr)_p/Al$ in situ composites. During the fabrication process, a low frequency electromagnetic field (EMF) is employed to improve the conditions of in situ chemical reaction between reactants powder and melt. Furthermore, during the direct chill casting process of composites melt the custom-designed electromagnetic fields are introduced to control the microstruc-

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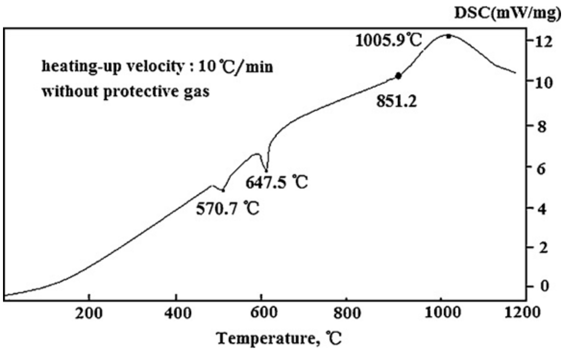

Fig. 1. The DSC curve of Al–Zr(CO_3)$_2$ components.

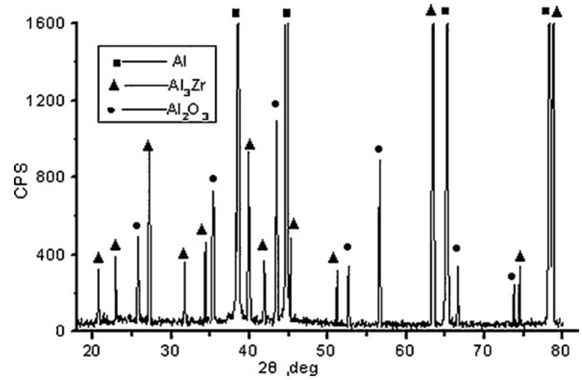

Fig. 2. The XRD diagram of composites fabricated with Al–Zr(CO_3)$_2$ components.

tures and improve the billet surface quality. The custom-designed electromagnetic fields are combined with a low frequency electromagnetic field and a high frequency electromagnetic field. The effect of electromagnetic fields on the microstructures, billet surface quality and the tensile properties of composites are studied. The mechanism of combined electromagnetic fields action is further investigated.

2. Experimental procedure

The raw materials were pure aluminum ingots (99.97%Al) and zirconium carbonate (Zr(CO_3)$_2$·$n$$H_2O$). Firstly, the zirconium carbonate powder was preheated to dehydrate in an electric drying oven at 250 °C for 3 h. Then the dried powder was cooled, grounded and screened, the particle size of which was less than 74 μm. At the same time, the aluminum ingot was melted in an electric furnace under argon atmosphere and held at 850 °C. The dehydrated reactants powder with the weight ratio 15 wt.% to the total aluminum melt was added into metal. During the in situ chemical reaction, the low frequency EMF was turned on. The input current was 0–750 A and the frequency was 0–15 Hz. The maximum magnetic induction intensity, B, was 0.1 T (Tesla). The melt was stirred with the electromagnetic force. The in situ reinforced particulates formed in the molten aluminum. The designed weight fraction of reinforcing particulates (Al_2O_3 and Al_3Zr) were 10 wt.%. After holding the reaction temperature at 850 °C for 30 min, the molten metal of PRAMCs was degassed and deslagged. Subsequently the molten metal was cast at 720 °C into round billet via semi-continuous direct chill casting process. During the casting process, the custom-designed electromagnetic fields, which were combined with a low frequency electromagnetic field and a high frequency electromagnetic field, was exerted on mold region. The frequency and input current of low frequency EMF were in the range of 0–15 Hz and 0–500 A, respectively. The frequency and power of the high frequency EMF generator were 20 kHz and 30 kW, respectively.

The differential scanning calorimeter (DSC, STA449C, Germany) was used to test the calorific effects of the in situ chemical reaction process. The X-ray diffraction (XRD, Rigaku D/max 2500) was employed to analyze the kinds of reinforcement phases. Scanning electron microscope (SEM, JEOL-JXA-840A) was used to observe the morphology of reinforcement phases. The volume fraction of particulates was determined through Image II professional package. Furthermore, MM-6 horizontal microscope was employed to determine the grain size of the composites samples corroded by 0.5 wt.% HF. Tensile behavior of composites at room temperature was measured with WD10 type electronic stretcher. The strain rate was 1×10^{-4} to 1×10^{-1} s^{-1}.

3. Results and discussion

3.1. Thermodynamic and kinetic analysis of in situ chemical reaction

Fig. 1 shows the DSC curve of Al–Zr(CO_3)$_2$ components. It can be clearly seen that there are two endothermic valleys at 570.7 °C and 647.5 °C, which demonstrate the zirconium carbonate decomposing and aluminum melting, respectively. More important, the calorific effect appears markedly when the temperature arrives at 851.2 °C, which indicates that an exothermic reaction takes place. Moreover, the utmost temperature arrives at 1005.9 °C.

The metallurgical reactions between Zr(CO_3)$_2$ powder and molten aluminum are deduced. The first step is the decomposition of Zr(CO_3)$_2$. The resultants are ZrO_2 and CO_2. Therefore, the second step is the thermit reaction between ZrO_2 and molten Al, which is shown as formula (1):

$$3ZrO_2 + 13Al = 3Al_3Zr + 2Al_2O_3 \tag{1}$$

According to Ref. [8], the standard Gibbs free energy, ΔG^{Θ}, of formula (1) is obtained:

$$\Delta G^{\Theta} = -1000065.4 + 756.8T \quad (\text{J mol}^{-1}\,\text{K}^{-1}) \tag{2}$$

In the reaction system, the melting points of ZrO_2, Al_3Zr and Al_2O_3 are 2600 °C, 1350 °C and 2046 °C, respectively. Therefore they are all solid state when the system temperature is lower than 1006.7 °C. On the nonstandard conditions, the Gibbs free energy of reaction (1) can be expressed as:

$$\Delta G = \Delta G^{\Theta} + RT\ \ln Q \tag{3}$$

where Q is the activity item. It is expressed as:

$$Q = \frac{a_{Al_3Zr}^3 \cdot a_{Al_2O_3}^2}{a_{ZrO_2}^3 \cdot a_{Al}^{13}} \tag{4}$$

If pure substance is selected as standard condition, all of the activities of Al_3Zr, Al_2O_3, ZrO_2 and Al are equal to 1 and then the Q is identically equal to 1. So:

$$\Delta G = \Delta G^{\Theta} = -1000065.4 + 756.8T \quad (\text{J mol}^{-1}\,\text{K}^{-1}) \tag{5}$$

The thermit reaction is an exothermic one. The equilibrium temperature is 1322.8 K (1049.7 °C). It will take place when the system temperature is lower than 1049.7 °C. Actually, the measured reaction system temperature varies from 870 °C to 1007 °C. It can be asserted that the thermit reaction can proceed spontaneously in the temperature range of experiment.

Fig. 2 is the XRD diagram of composites in situ fabricated with Al–Zr(CO_3)$_2$ components. It reveals that Al_2O_3 and Al_3Zr are the only resultants in the composites except Al matrix. This indicates that Al_2O_3 and Al_3Zr reinforcement phases have been obtained.

Furthermore, according to the analysis of thermodynamic process for the in situ chemical reaction it can be seen that the contacts between reactants are the prerequisite for in situ chemical reaction. After Zr(CO_3)$_2$ particulates enter into the melt and decompose as ZrO_2 and CO_2, the molten aluminum reaches the outer boundary layer of ZrO_2 particulates through diffusion and convection. When molten aluminum adhere to the surface of ZrO_2 the thermit reaction will take place instantly. Subsequently the reinforced phases Al_2O_3 and Al_3Zr generate in matrix. With the proceeding of in situ chemical reaction, the crystal nuclei of reinforced phases grow up and disperse in matrix.

When there is no electromagnetic stirring, the mass and heat transfer and the diffusion proceed depending on their gradients. The transmission speeds are rather low. When imposed on electromagnetic stirring the diffusion and mass transfer of reactants

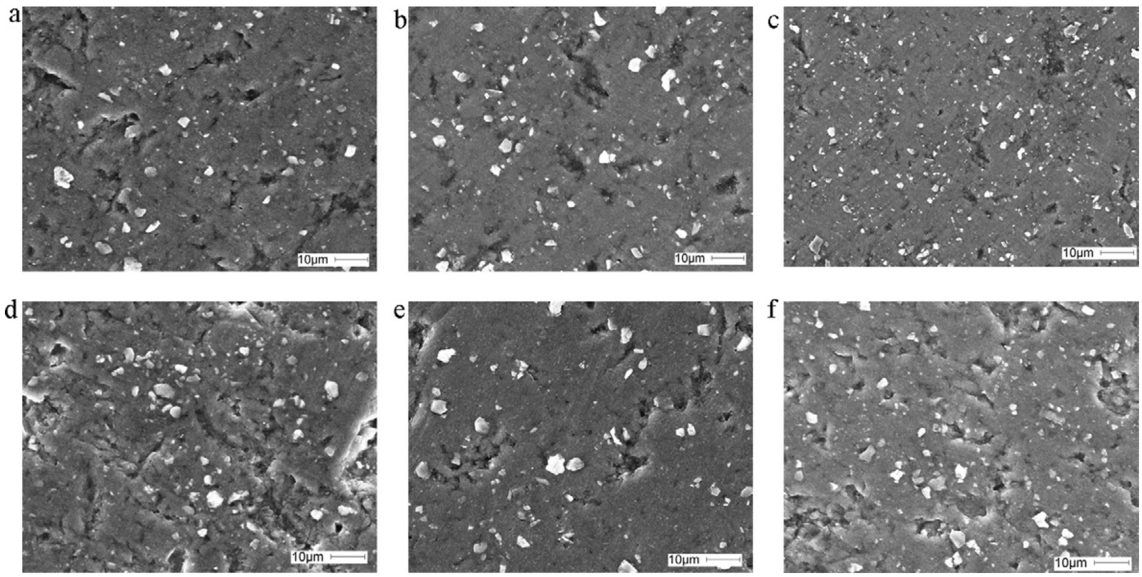

Fig. 3. Microstructure of $(Al_2O_3+Al_3Zr)_p$/Al composites synthesized without and with electromagnetic stirring: (a) without EMS; (b) 100 A, 3 Hz, B = 0.013 T; (c) 150 A, 4 Hz, B = 0.025 T; (d) 200 A, 5 Hz, B = 0.029 T; (e) 250 A, 6 Hz, B = 0.027 T; (f) 300 A, 7 Hz, B = 0.028 T.

are accelerated, which improves the kinetic conditions of fabrication [9]. In the process of particulates nucleation and growth, the enhanced heat and mass transfer is favorable to increasing the contact opportunities of matrix and solid ZrO_2 and the generating probability of reinforced phases adds up. Meanwhile, electromagnetic field imposes on the melt in the form of electromagnetic wave, which augments the structural and energy fluctuations in inner melt and decreases the critical nucleating power to a certain extent [10]. This effect attributes to the nucleation of Al_2O_3 and Al_3Zr particulates. In the last diffusion stage the stirring action can accelerate the mix of aluminum matrix and reinforced particulates, which promotes the distributions of the reinforced particulates in Al matrix.

The suitable electromagnetic induction intensity (B) is the most important factor to control the in situ fabrication process. If it is too low the stirring action is not enough. However, if it is too high the particulates will segregate in matrix. Fig. 3 is the microstructure of $(Al_2O_3+Al_3Zr)_p$/Al composites in situ fabricated without and with electromagnetic stirring. As shown in Fig. 3(c), when the B is 0.025 T (the corresponding current and frequency of electromagnetic field is 150 A and 4 Hz), the particulates are well distributed in matrix. Meanwhile the volume fraction of particulates fabricated with electromagnetic stirring is also increased. Moreover, the sizes of particulates tend to be uniform, the ranges of which are 1–2 μm.

3.2. Design and principle of CEMF-DC casting process

The CEMF-DC casting (direct chill casting under custom-designed electromagnetic fields) process is put forward according to the action mechanism of electromagnetic fields on the solidifying process of in situ composites melt. The custom-designed electromagnetic fields are combined with a low frequency electromagnetic field and a high frequency electromagnetic field. In which, the low frequency electromagnetic field is used to control the sizes of particulates and matrix grains and promote the particulates distribution in matrix, so as to improve the inner quality of composites. In the meantime, the high frequency electromagnetic field is employed. The electromagnetic pressure of which is exerted to improve the billet surface quality. The action mechanism of high frequency electromagnetic field on billet surface quality has been analyzed detail in Ref. [11]. Fig. 4 is the schematic diagram showing the CEMF-DC casting process. Table 1 is the technical parameters of CEMF-DC casting process.

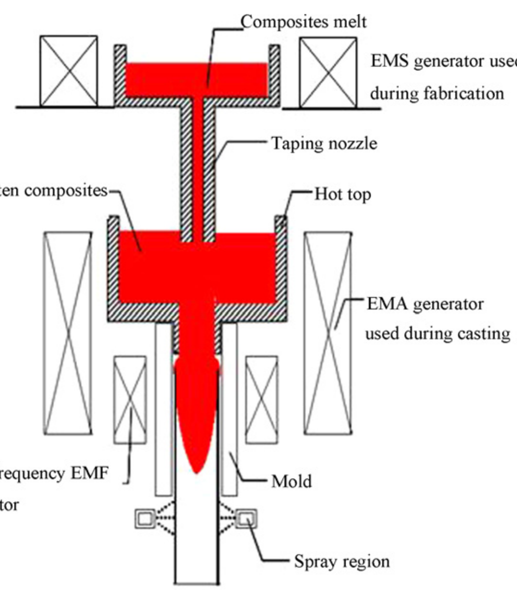

Fig. 4. The schematic diagram of CEMF-DC casting process.

3.3. The microstructure and surface quality of composite billet

Fig. 5 indicates the microstructure of the composites billet prepared by CEMF-DC casting process. The output current of the high frequency EMF is fixed 80 A. As shown in Fig. 5(a), there are fewer

Table 1
The technical parameters of CEMF-DC casting process.

Liquid melt	15 vol.% $(Al_3Zr+Al_2O_3)_p$/A356
Output frequency of low frequency EMF [Hz]	4
Output current of low frequency EMF [A]	150
Output current of high frequency EMF [A]	0–80
Casting temperature (°C)	710–720
Diameter of round billet (mm)	60

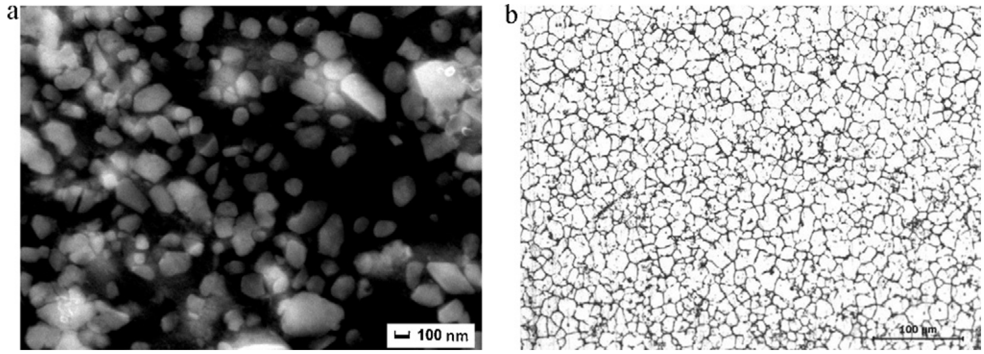

Fig. 5. Microstructure of composites fabricated by CEMF-DC method (a) distribution and sizes of particulates and (b) grain size of matrix in composite.

casting defects. The average sizes of particulates are in the range of 0.5–1 μm. More importantly, the particulates distribute uniformly in the matrix. Fig. 5(b) demonstrates the effect of the combined electromagnetic fields on the grain size of matrix. The grain size of matrix is in the range of 20–40 μm, whereas the matrix grain size of composites fabricated with conventional process without electromagnetic field is about 70–80 μm. As a conclusion, the particulates and matrix grains can be fined remarkably as well as the dispersion of particulates is improved by this method. These results are mainly due to the electromagnetic stirring force during the casting process.

Fig. 6 shows the variations of billet surface quality with the output current of high frequency EMF. It is seen that the billet surface quality can be improved remarkably by high frequency EMF. Moreover, when the output current of high frequency EMF is increased to 80 A, the billet surface has the best quality, as shown as Fig. 6(e), the billet surface is very smooth. Furthermore, there is no any defect on the billet surface. Under the high frequency electromagnetic field the electromagnetic force is vertical to the casting direction and towards the center of billet. Because the skin depth of high frequency electromagnetic field is very thin, the electromagnetic force concentrates on the surface of billet. The force not only counteracts the rotational centrifugal force, but also decreases the contact pressure between the initial solidifying billet and mold. The soft contact status appears between the billet shell and mold and therefore the resistance tends to be zero. As a result, the billet surface quality is improved greatly by the high frequency electromagnetic field.

3.4. Tensile property of composites

When the theoretical weight fraction of particulates is 10 wt.% the tensile strength of composites in situ fabricated without EMS is 150.3 MPa while that fabricated with 0.025 T EMS is 254.6 MPa, which is increased by 69.4%.

The important reason is that the actual volume fractions of reinforced particulates are increased, which helps the reinforced particulates composites display strengthening effects. The Orowan and grain-refined strengthening are regarded as the main action mechanisms of particulates reinforced aluminum matrix composites. The plastic deformation of the material is caused when the composite bear external load. Orowan strengthening results from the interaction between the dislocations and the dispersed particulates. The hard reinforced particulates, Al_3Zr and Al_2O_3, act as the obstacles to hinder the motion of dislocations near the particulates. This strengthening effect is enhanced gradually with the increasing volume fraction of particulates [12,13]. Secondly, the grain size of matrix and structure are the key factors to influence the mechanical properties of materials. When there are direction relationships between reinforced phases and matrix, the surface of reinforced particulates will become the basements for heterogeneous nucleation during solidification. It increases the nucleation ratios and refines the grains of matrix. In fact there exists matching relations between Al_3Zr and Al matrix in $(Al_3Zr + Al_2O_3)_p$/Al composites. They are $[1\,0\,0]_{Al_3Zr}//[1\,0\,0]_{Al}$, $(0\,0\,1)_{Al_3Zr}//(0\,0\,1)_{Al}$, the misfit degree is only 0.95% [14]. So Al_3Zr can act as the basements when the composite melt solidifies. More volume fraction and more

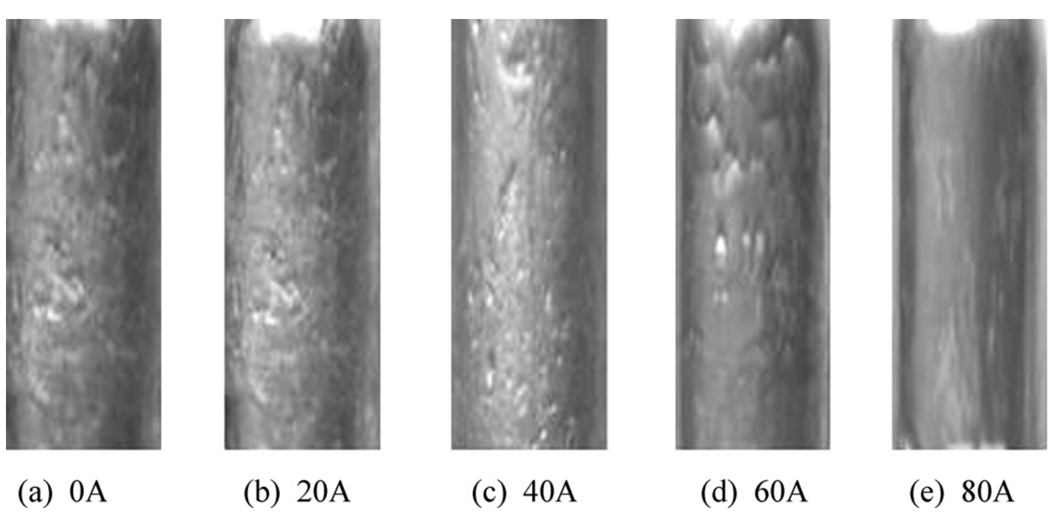

Fig. 6. Improvement of billet surface quality with output current of high frequency EMF.

uniform distribution of Al_3Zr particulates will strengthen the grain refining effect.

4. Conclusions

$(Al_2O_3 + Al_3Zr)_p$/Al composites were fabricated from Al–15 wt.% $Zr(CO_3)_2$ systems via in situ chemical reaction at 850 °C. A low frequency electromagnetic field is employed to the composites melt during the process of in situ chemical reaction to improve the conditions of reaction between reactants powder and melt. The optimized electromagnetic density of low EMF is 0.025 T. In the direct chill casting process of composites melt, the custom-designed electromagnetic fields are introduced to control the microstructures and improve the billet surface quality. The qualities of composites billet, including microstructure, billet surface quality and tensile property are improved remarkably.

1. Microstructure analysis by SEM indicates that the in situ reinforcement particulates are distributed uniformly in the aluminum matrix, the average size of the reinforcement particulate is 0.5–1 μm and the grain size of aluminum matrix is fined to 20–40 μm. This was because that the Lorenz force improved the kinetic condition and accelerated the nucleation of endogenetic particulates.
2. Due to the electromagnetic pressure of high frequency EMF, the surface quality of round billet is remarkably improved. When the output current of high frequency EMF is 80 A, the billet has the best surface quality.
3. The tensile strength of composites in situ fabricated with EMS is 254.6 MPa, which is increased by 69.4% compared with those of composites in situ fabricated without electromagnetic field. The strengthening mechanisms involve Orowan strengthening and grain refining strengthening.

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