Formation of In-Situ Dispersion Strengthening Particles in Cast FeCrAl Alloy

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Abstract: In order to fabricate dispersion strengthened alloys strengthened by submicron-sized or nano-sized stable particles through casting routes, understanding of the formation process of dispersion strengthening particles in metal melt is of significance. Thus, nano NiO and TiO_2 particles were selected as reactant to form in-situ dispersion strengthening oxide particles in Fe20Cr5Al alloy. Nano NiO and TiO_2 particle powder was separately dispersed into nano Ni powder first. The loose mixed nano powder was added in Fe20Cr5Al alloy melt when pouring the melt into mold. The study shows that nano NiO particles were not as effective as nano TiO_2 particles in forming dispersion strengthening Al_2O_3 particles. The final diameters of dispersion strengthening oxide particles arose from nano TiO_2 particles were of submicron. The Brownian collision of particles had caused this coarsening.

Key words: in-situ particle; dispersion strengthening particle; formation; cast FeCrAl alloy

The mechanisms responsible for the formation of in-situ reinforcements have been widely studied in the development of particles reinforced metal matrix composites produced by casting routes[1-2]. In order to fabricate submicron or nano-sized particles strengthened composites or dispersion strengthened alloys through casting routes[3-5], understanding of the formation mechanisms of dispersion strengthening fine particles in metal melt is of significance. In present work, nano-sized oxides were selected as reactant to form dispersion strengthening particles in Fe20Cr5Al melt. The behaviors of these nano-sized oxides of great number density in steel melt were studied.

1 Experimental

The investigations of oxide dispersion strengthened alloys produced by powder metallurgy routes show that the oxides mass percent of 0.5% — 1% and oxides size of about 30 nm are ideal parameters (the particles number density is of about 10^{20} m^{-3}) to achieve the best mechanical properties combination[6]. In present experiments, the average diameter of original particles is about 30 nm (measured by small angle scattering method) and the mass percent of the oxides powder added into testing alloys is about 0.5% and the chemical composition of the testing alloys are shown in Table 1. NiO was selected as an unstable oxide and TiO_2 (rutile) was selected as a stable oxide (more stable than oxides of iron and chromium, but less stable than Al_2O_3). Because of the presence of 5% Al (in mass percent) in the melt, these oxides should be reduced to Al_2O_3 after entering into melt. In this study, the following two issues are intended to be clarified: firstly, which oxide is more effective as the nuclei of forming nano-sized or ultrafine Al_2O_3 particles; secondly, whether the newly formed Al_2O_3 particles keep the same size of the nano reactant particles.

Because nano oxide particles are easily agglomerated, dispersion agent is needed. Nano-sized Ni powder was selected as the dispersion agent. Nano Ni powder and nano oxide powder were blended in acetone with ultrasonic stirring, and then the mixed nano powder was dried.

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Table 1　Nominal chemical composition of the test alloy　　　　(mass percent, %)

Alloy No.	Base			Oxide powder		Dispersion agent
	Fe	Cr	Al	Nano NiO	Nano TiO₂ (rutile)	Nano carbonyl Ni
1#	Balance	20	5	0.5	—	1.5
2#	Balance	20	5	—	0.5	1.5

The prepared loose mixed nano powder was charged into steel mold and the mold was set into vacuum chamber before vacuum induction melting. Base alloy was melt in a vacuum induction furnace using pure iron, pure chromium and pure aluminum. The melting point of base alloy is about 1500 ℃, and the pouring temperature was 1580 ℃. The alloy melt solidified in several seconds after pouring. Each steel ingot was in the mass of about 4 kg.

Samples for metallographic observation and extraction of oxides were machined by electric discharge machining from the different ingot areas. The specimens for microstructure examination cut from the cast ingots were ground, polished and chemically etched with 10 mL HF + 10 mL HNO₃ + 80 mL H₂O solution. Hydrochloric acid solution (HCl : H₂O=1 : 4) was used to extract oxides in the testing alloys. SEM equipped with EDS system was used to reveal microstructure details and phase composition.

2　Results and Discussion

2.1　Ni and Ti distribution at macroscopic scale

Table 2 shows the average Ni and Ti content of the three different parts of the ingots [EDS (energy dispersive spectrometer) average composition analysis on surface at the magnification of 100]. Some powder was splashed and lost in the pouring process, so the amount of nano powder that entered into steel stream was less than that charged into the mold. Element Ni is uniformly distributed in both alloys samples. The uniformity of the Ti distribution (the indicator of the presence of TiO₂) was poor at macroscopic scale. Some parts of the ingots had no Ti distribution. This was a shortcoming of the process.

Table 2　The Ni and Ti contents in three
different areas　(mass percent, %)

| Area No.	1# alloy	2# alloy	
	Ni	Ni	Ti
1	0.56	0.45	0.12
2	0.62	0.70	0
3	0.58	0.91	0.1

2.2　Oxide distribution at microscopic scale

Fig. 1 shows the typical oxides found in 1# alloy samples. Cluster-like phases in Fig. 1 (a) are Al₂O₃. The tube-like phase in Fig. 1 (b) contains Al, O and N through the EDS analysis, but the exact identity is not clear. The fine particles of about 0.5 μm in Fig. 1 (b) are Al₂O₃ granules, which was verified by shape and EDS chemical composition analysis of extraction residua as shown in Fig. 1 (c) and (d).

Fig. 2 (a) shows the dispersion strengthening oxides distribution in 2# alloy samples. EDS chemical composition analysis shows that Ti and Ni exist in this area. This suggests that those oxides are relative with the intentionally added nano TiO₂ powder. The average diameter of the oxides is in the range of 0.1—0.3 μm, which is larger than the initial oxides diameter (about 30 nm). Fig. 2 (b) shows the chemical composition of the extraction residua. It shows that TiO₂ particles were partially reduced by Al in the steel melt.

Fig. 3 shows a casting defect surface of 2# alloy. Spherical particles of different sizes are found on the surface. Table 3 shows the chemical composition of two large spherical particles. The spherical particles are not pure oxide particles but the mixture of base alloy and oxides. This suggests that when nano powder agglomerate contacted with steel stream, steel melt infiltrated into the space between nano particles. This mechanism is in favor of the nano oxide particles entering into steel stream.

2.3　Discussion

According to the design in this study, when the mixed nano powder meets the high temperature molten steel stream, nano nickel particles will melt and be mixed into steel stream, and the nano oxide particles which dispersed in nano nickel powder will also disperse into steel stream. According to the Gibbs free energies of oxides formation, the following reactions will exist:

$$(NiO)_x + [Al] \rightarrow [Ni] + (Al_2O_3)_s \qquad (1)$$

$$(TiO_2)_x + [Al] \rightarrow [Ti] + (Al_2O_3)_s \qquad (2)$$
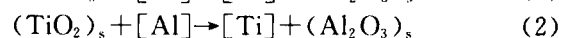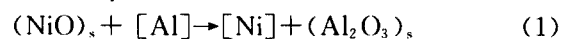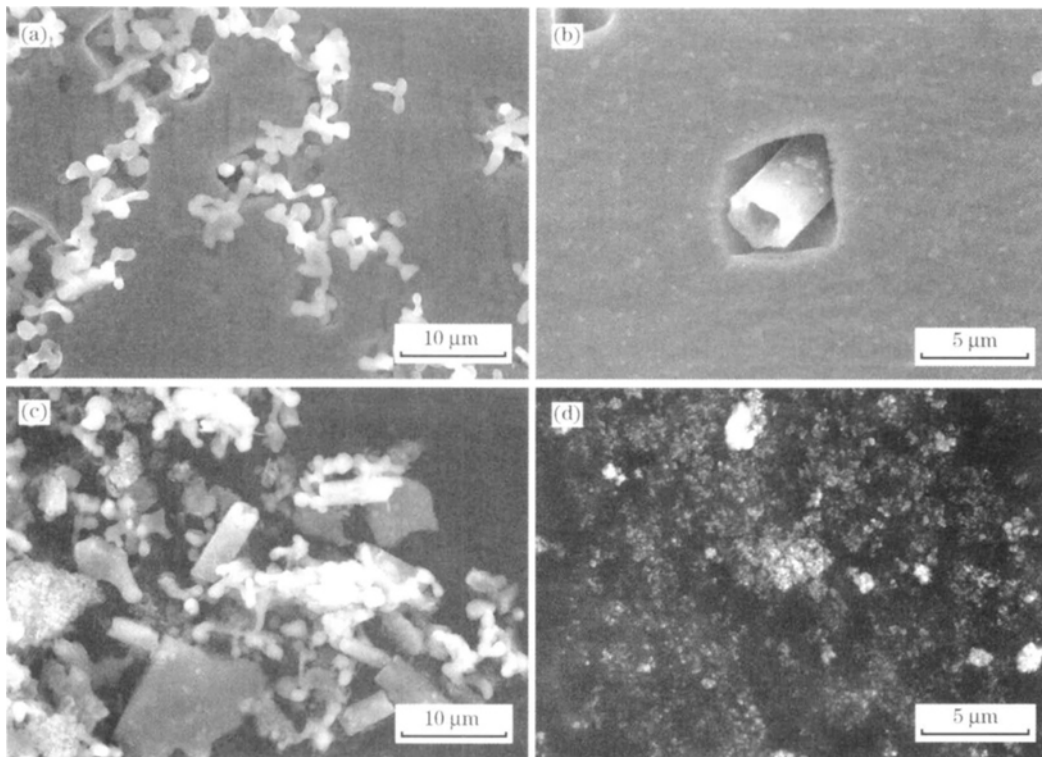
(a) Cluster-like Al₂O₃ found in 1⁼ alloy;　(b) Tube-like phase and fine Al₂O₃ granules found in 1⁼ alloy;　(c) Extracted residua containing cluster-like and tube-like phases of 1⁼ alloy;　(d) Extracted residua containing fine Al₂O₃ granules of 1⁼ alloy.

Fig. 1　Oxides found in 1⁼ alloy
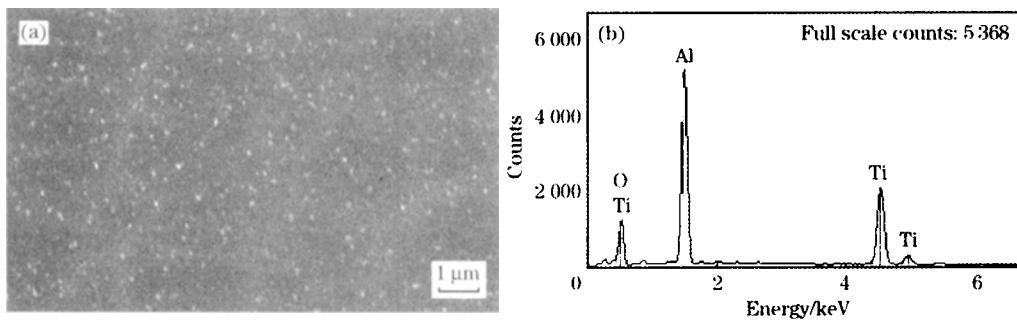
(a) Distribution of oxide particles in 2⁼ alloy;　(b) Chemical composition of extracted residua of 2⁼ alloy.

Fig. 2　The oxides distribution and chemical composition of the oxides found in 2⁼ alloy
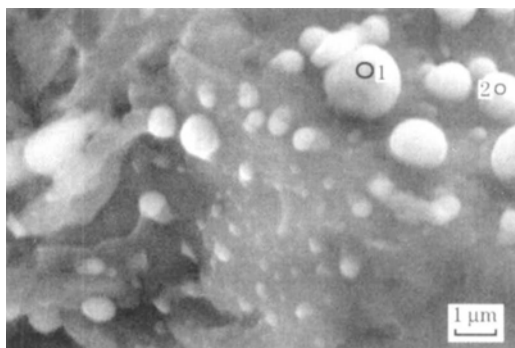
**Fig. 3　One casting defect surface of 2⁼ alloy with spherical particles on it**

As shown in Fig. 1 (b) and Fig. 2 (a), nano NiO particles were not as effective as TiO_2 to form dispersed Al_2O_3 granules. In contrast, the NiO powder caused the appearance of micron-sized cluster-like and tube-like Al_2O_3 in 1⁼ alloy and the size of the fine Al_2O_3 granules arose from NiO was larger than that

Table 3　Composition of spherical particles in Fig. 3

(atomic percent, %)

Element	O	Al	Ti	Cr	Fe	Ni
Particle 1	7.38	12.50	2.82	16.60	58.64	2.06
Particle 2	12.83	15.38	2.88	14.42	52.54	1.95

arose from TiO_2. Because NiO is less stable than TiO_2, reaction (1) may consist of the following two reactions:

$$(NiO)s \rightarrow [Ni] + [O] \qquad (3)$$

$$[O] + [Al] \rightarrow (Al_2O_3)s \qquad (4)$$
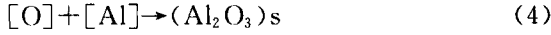
Namely, NiO decomposed first. Oxygen atoms in the melt quickly diffused toward the few existing Al_2O_3 nuclei. Al_2O_3 nuclei can grow to micron-sized in seconds by this "diffusion-growth" mechanism[7]. This can explain the appearance of micron-sized Al_2O_3 in 1# alloy.

Stable oxide TiO_2 did not decompose in high temperature melt. They dispersed into melt as solid nuclei and oxygen source for the formation of more stable Al_2O_3 particles. Aluminum atoms in the melt diffused toward the TiO_2 particles and reduced the TiO_2 into Al_2O_3 gradually. The reduction reaction (solid-liquid reaction) rate was limited and the reaction time (from start pouring to solidification finish) was limited, so the TiO_2 particles were only partially reduced.

Then the second issue arises: why the final dispersion strengthening particles (partially reduced TiO_2 particles) size in 2# alloy is still larger than the initial particles size? It is well known that the finer the oxides are, the better the effect of dispersion strengthening. The growth of oxide particles should be prevented or controlled.

For the average diameter of oxides particles is below micron, the behavior of these particles should be governed by Brownian motion. Brownian motion causes fine particles to spread and causes particles growth by collision between particles. The first effect is in favor of achieving dispersion strengthening and the second effect hinders the realization of dispersion strengthening through casting route.

The average square displacement $\overline{x}^2$ of the fine particles can be calculated by the following equation[8]:

$$\overline{x}^2 = \frac{2kT}{\alpha}t = 2D_p t \qquad (5)$$

where, k is Boltzmann constant $k = 1.38 \times 10^{-23}J \cdot K^{-1}$; T is thermo-dynamical temperature, K; t is time, s; α is resistance coefficient caused by viscosity, $\alpha = 6\pi r\eta$; r is the average radius of particles; η is the viscosity coefficient of the melt, $N \cdot s/m^2$; and D_p is the "diffusion" coefficient of the particles, $D_p = kT/\alpha$.

In this experiment, the average square displacement can be estimated as follows: assume the temperature T is 1853 K, r is 30 nm and η equals to $6.1 \times 10^{-3}N \cdot s/m^2$, then the particle average square displacement in one second $\overline{x}^2 = 1.5 \times 10^{-11}m^2$ ($\sqrt{x^2} = 3.87 \times 10^{-6}$ m) is achieved. This means that Brownian motion assure the uniformity of particle distribution in the range of several micron as seen in Fig. 1 (b) and Fig. 2 (a).

The particles number density $N(t)$ varies with time can be calculated by the following equation proposed by Smoluchowski[9]:

$$N(t) = \frac{N(0)}{1 + 8\pi D_p rN(0)t} \qquad (6)$$

The relationship between particles number density $N(t)$ and the particles average diameter $d(t)$ can be calculated by the following equation:

$$N(t) = \frac{6}{\pi} \frac{\rho_1}{\rho_2} \frac{f_w}{d^3(t)} \qquad (7)$$

where, ρ_1 is the melt density; ρ_2 is the oxide density; and f_w is the mass fraction of the oxides in the melt.

In present experiment, $N(0)$ is about 10^{20} m^{-3}. Assume the same D_p and r as before, $\rho_1/\rho_2 = 2$, $f_w = 0.002$ and the $N(t)$ and $d(t)$ curves are shown in Fig. 4.

Fig. 4 shows that because of the presence of Brownian collision, a large number of nano oxide particles in steel melt will grow to 300 nm in 1 s from the original diameter of 30 nm. Considering the temperature of melt dropped quickly and the viscosity of the melt rose after pouring, the practical time might be a little longer. This explains why the final diameters of dispersion strengthening oxide particles in 2# alloy were in the range of 100−300 nm. Some measures, such as increasing melt viscosity, introducing ultrasonic stirring into the melt[4] and so on, should be adopted to reduce or counteract the effect of
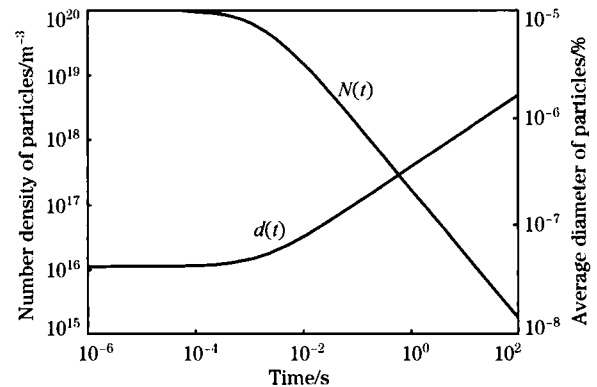

Fig. 4   Variation of $N(t)$ and $d(t)$ with time caused by Brownian collision

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Brownian collision.

3 Conclusions

1) Nano NiO decomposed first after entering steel melt. The oxygen atoms diffused to a few Al_2O_3 nuclei and the process promoted the appearance of micron-sized Al_2O_3. A certain number of Al_2O_3 granules of about 0.5 μm were formed in the melt. Nano NiO (unstable oxide) particles were not effective nuclei of forming dispersion strengthening Al_2O_3 granules.

2) Nano TiO_2 particles dispersed into melt were partially reduced by aluminum. Nano TiO_2 particles were more effective nuclei of forming dispersed Al_2O_3 granules, compared with nano NiO particles. But the average diameter of final oxides was still larger than the initial particle diameter. The newly formed oxides had coarsened.

3) Brownian collision caused the newly formed nano oxide particles to grow to submicron-sized in seconds. Measures such as ultrasonic stirring are needed to keep the nano oxides particles separate.

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