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Experimental study and thermodynamic modeling of the Al-Sc-Zr system

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ABSTRACT

As a typical system in the family of heat-resistant aluminum alloys, the Al-Sc-Zr ternary system was thermodynamically studied by experimentation and theoretical calculation. Employing the scanning electron microscopy/energy dispersive X-ray spectroscopy and X-ray diffraction, the isothermal section at 873 K was determined with equilibrated alloys. Two stable ternary compounds $Al_{75}Sc_{16}Zr_9$ and $Al_{75}Sc_{10}Zr_{15}$ were newly discovered. By means of the differential scanning calorimetry, phase transformation temperatures of selected samples were obtained. In addition, the as-cast microstructure of individual alloys was observed to identify the primary crystallization phase during solidification. Based on the experimental information mentioned above, the Al-Sc-Zr system was thermodynamically optimized combining the first-principles calculation and the CALPHAD method, with the constituent binary system Sc-Zr optimized for the first time. Using the thermodynamic parameters obtained in this work, the isothermal section, vertical section and liquidus projection were all calculated and then compared with available experimental data, most of which could be accounted for satisfactorily.

1. Introduction

Scandium, both a rare earth element and a transition element, is known as the most outstanding alloying element in aluminum alloys. The addition of a little amount of it can significantly improve the mechanic properties at elevated temperatures [1–3], which greatly promotes the development of heat-resistant aluminum alloys and enlightens the studies afterwards on mechanisms and methods of strengthening of Al-based alloys. The strengthening effect of Sc stems from the precipitation of the Al_3Sc phase, the one possessing an $L1_2$ structure that is coherent with the matrix. These fine particles of Al_3Sc have a high thermal stability and effectively impede the motion of dislocations, grain boundaries and subgrain boundaries, thus raising the recrystallization temperature and the creep resistance. However, due to the high price of Sc, the Sc-containing aluminum alloys are mostly applied in the fields of national defense and military industry as structural materials and in the upscale civilian products. In order to expand their application, it is extremely necessary to pursue the low-cost substitutes [4–6].

Numerous studies have proved that superior mechanic properties will be obtained at high temperatures in the Sc-containing aluminum alloys where Zr is used to replace Sc partially than in the Zr-free ones [7–12]. The combined addition of Sc and Zr in the Al matrix promotes the formation of egg-shell shaped nanoparticles $L1_2$_Al_3(Sc, Zr), with the egg-part being rich in Sc and the shell-part rich in Zr [13]. The Zr-rich shell prevents the transport of the atoms due to its slow diffusion, which retards the coarsening rate and improves the thermal stability and creep resistance. In view of the importance of Sc and Zr to the heat-resistant aluminum alloys, the phase relations of the Al-Sc-Zr system need to be deeply investigated and clearly understood. With this aim, the ternary system was experimentally studied and thermodynamically optimized. A reasonable thermodynamic description was established finally. Hopefully, this work would provide guidance for upgrading current commercial heat-resistant aluminum alloys and developing novel materials.

2. Review of the Sc-Zr and Al-Sc-Zr systems

Beaudry and Daane [14] have investigated the Sc-Zr binary phase diagram by means of differential scanning calorimetry

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(DSC), with the solidus determined and the liquidus not. Only three solid solution phases exist, including liquid, bcc_A2 and hcp_A3, and not a binary compound was reported. The transformation temperature between bcc_A2 and hcp_A3 phases reaches a maximum point at ~29 at.% Zr. Based on these experimental results, Palenzona and Cirafici [15] made a review on this phase diagram, where they adjusted the melting points and transformation temperatures of pure Sc and Zr to be the values that are now widely accepted.

For the Al-Sc-Zr ternary system, the only available experimental information at present is the isothermal section at 773 K, studied by Sokolovskaya et al. [16] with equilibrated alloys. The arc-melted samples were first annealed at 773–973 K for 110 h, and then at 773 K for 400 h. The temperature for the first-order homogenizing annealing depends on the alloy compositions. According to the experimental results, there is a three-phase field consisting of Al_3Sc, Al_3Zr and Al in the Al-rich region. The Al_3Sc and Al_3Zr compounds occupy a certain area in the ternary phase diagram, for which the contents of Al vary instead of a constant value 75 at.%. With the increase of the content of Zr, the Al_2Sc phase extends into the interior of the composition triangle at a direction of reducing the Al content. Since the $AlSc_2$ and $AlZr_2$ have the same crystal structure, i.e., the Ni_2In type structure, continuous solid solution was reported to be formed. Except $AlSc_2$ and $AlZr_2$, AlZr has the largest homogeneity range, with a maximum solubility of 25.0 ± 5.0 at.% Sc, followed by Al_2Sc, where 15.5 ± 1.5 at.% Zr at most could be dissolved.

3. Experimental procedure

With 99.99 wt.% purity of Al, Sc and Zr as starting materials, twenty individual alloys, 4 g for each, were arc melted under the protection of argon. Their nominal compositions are listed in Table 1. Using Ti ball as the oxygen getter, all the alloys were melted four times and flipped after each round to ensure homogeneity. Since Sc is volatile, the composition of each sample was measured by energy dispersive X-ray spectroscopy (EDX), as is also given in Table 1. Comparing the nominal and measured alloy compositions, it can be seen that the difference becomes larger with the increase of the content of Sc, while that for the Al-rich samples is very small.

The as-melted samples were all divided into two pieces. One of them was examined by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) to have the as-cast microstructure observed and the primary crystallization phase during solidification identified. Another piece was first sealed in the vacuumed and argon refilled quartz tube and then put in the diffusion furnace at 873 K for 1440 h, followed by a water quench. The annealed samples were cut into pieces again to be examined by SEM/EDX, X-ray diffraction (XRD) and DSC. The annealed microstructure was observed on the FEI Quanta-200 SEM and the compositions of constituent phases were analyzed by EDX, with an accelerating voltage of 20 kV and a beam spot of 5.0 or 6.0 Å. Using the Cu Kα radiation, the XRD experiments were carried out on the D/Max2500DC equipment. It scanned from 10° to 90° at a rate of 8°/min, with the voltage and the current being 40 kV and 250 mA, respectively. Bulk samples were prepared for the XRD examination when the alloys are hard and ductile, while powder ones were used when they are brittle. Ten samples, namely 1-4#, 14# and 16-20#, were selected to be tested on the NETZSCH STA 449C DSC equipment. They were heated from room temperature to 1400 °C at a rate of 10 K/min and then cooled to 200 °C at the same rate, except that the 1-3# samples were heated to 1300 °C. Both the reference and the sample were placed in the Al_2O_3 crucibles covered with a lid. During the whole heating and cooling process, argon flows through the chamber continuously to protect the samples from oxidation.

4. Calculation methods

4.1. Thermodynamic modeling

For pure elements, the Gibbs energy was adopted from the SGTE unary database [17]. The substitutional solution model was employed to describe the solution phases in the Sc-Zr and Al-Sc-Zr systems, namely liquid, hcp_A3 and bcc_A2. When establishing the thermodynamic database of the ternary system, a unified Gibbs energy expression was employed for $AlSc_2$ and $AlZr_2$ phases, since they both have the same crystal structure as Ni_2In. Other Al-Sc binary compounds, i.e., Al_3Sc, Al_2Sc and AlSc, and Al-Zr binary compounds, i.e., Al_3Zr, Al_2Zr, Al_3Zr_2, AlZr, Al_3Zr_4, Al_2Zr_3 and $AlZr_3$, have a certain solubility of the third component. Therefore, they

Table 1
Nominal compositions of individual alloys.

Alloy no.	Desired composition (at.)			EDX analyzed composition (at.)		
	Al	Sc	Zr	Al	Sc	Zr
1#	0.800	0.150	0.050	0.816	0.131	0.053
2#	0.800	0.086	0.114	0.778	0.085	0.137
3#	0.800	0.050	0.150	0.791	0.048	0.161
4#	0.691	0.270	0.039	0.726	0.217	0.057
5#	0.690	0.240	0.070	0.706	0.205	0.089
6#	0.688	0.172	0.140	0.700	0.138	0.162
7#	0.696	0.135	0.169	0.705	0.109	0.186
8#	0.631	0.102	0.267	0.638	0.084	0.278
9#	0.594	0.372	0.034	0.632	0.334	0.034
10#	0.560	0.290	0.150	0.586	0.265	0.149
11#	0.550	0.280	0.170	0.559	0.265	0.176
12#	0.445	0.203	0.352	0.507	0.143	0.350
13#	0.460	0.050	0.490	0.455	0.051	0.494
14#	0.420	0.290	0.290	0.415	0.228	0.357
15#	0.420	0.150	0.430	0.423	0.146	0.431
16#	0.376	0.362	0.262	0.387	0.246	0.367
17#	0.350	0.200	0.450	0.344	0.176	0.480
18#	0.350	0.050	0.600	0.352	0.054	0.594
19#	0.235	0.200	0.565	0.238	0.199	0.563
20#	0.180	0.050	0.770	0.182	0.055	0.763