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Redetermination of the Eutectic Composition of the Co-Sn Binary Alloy

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A series of Co-Sn alloys was solidified. It was found that the as-cast microstructure of the Co-20.5at.%Sn alloy, which on the basis of literature reports has long been thought to be the eutectic composition, contains much primary phase besides lamellar eutectics. The cooling curve of this alloy contains two exothermic peaks. In contrast, when a Co-24.0at.%Sn alloy was solidified, an entire lamellar eutectic was obtained in the as-cast microstructure. Also, the thermal analyses indicate that there is only one solidification reaction in this alloy. It is suggested that the actual eutectic composition of the Co-Sn system is around Co-24.0at.%Sn, and the corresponding eutectic temperature is about 1385 K.

Keywords Co-Sn, DTA, eutectic composition, microstructures

1. Introduction

A recently assessed Co-Sn phase diagram is shown in Fig. 1. In this diagram, the temperatures and key compositions of invariant reactions are given. In the Co-rich region of the Co-Sn phase diagram, the liquidus temperatures that correspond to the reaction $L \leftrightarrow \alpha(Co)$ were determined by thermal analysis over a composition range[1] of 0 to 20.5 at.% Sn. The solid solubilities of Sn in α(Co) were determined from results of activity measurements.[2] The congruent reaction $L \leftrightarrow \beta - Co_3Sn_2$ happens at 1170 °C, and its homogeneous compositions were estimated from activity data.[2] The eutectic reaction $L \leftrightarrow \alpha(Co) + \beta - Co_3Sn_2$ is an important reaction in Co-Sn system. It has been reported to occur at about 1112 °C, of a Sn concentration in the liquid of 20.5 at.% from thermal analysis data and activity measurements.[1]

Our recent experiments have found that a solely eutectic microstructure could not be obtained during solidification of the binary Co-Sn alloy with 20.5 at.% Sn. The raw materials used in the experiment were of high purities, i.e., 99.999 wt.% Co and 99.99 wt.% Sn. Preparation of Co-Sn alloy samples was carried out in 99.9999 pure Ar atmosphere and protected by a molten glass slag, which removes the influence of oxygen and other impurities. So it is unlikely that the noneutectic structure results from impurities. Murty and Kattamis[3] once studied the solidification structure of the highly undercooled Co-Sn eutectic alloy with the eutectic composition being 20.5 at.% Sn. They also observed that there existed spherical α-phase at the center of the lamellar eutectic region, and they thought it could be attributable to the remelting of the primarily formed α-phase that grew into the lamellar eutectic subsequently. The authors of the present paper thought it might be caused by an inaccurate eutectic composition of the Co-Sn alloy in the assessed phase diagram, and on this basis, the present study was undertaken.

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2. Experiments

As noted previously, the initial materials were of good purity and the experiments were designed for protection from contamination. A tentative experiment pointed to occurrence of the eutectic in the range 23 to 25 at.% Sn. Consequently, Co-Sn specimens with different compositions, Co-20.5at.%Sn, Co-23.0at.%Sn, Co-23.5at.%Sn, Co-24.0at.%Sn, Co-24.5at.%Sn, and Co-25.0at.%Sn were prepared. All of the alloy specimens were prepared in situ by a flux technique in a vacuum chamber backfilled with high-purity Ar atmosphere. The microstructures of the samples were observed by optical microscope (OM). For clear observation of the microstructures, the specimens were etched using a mixed solution of $CuSO_4$, HNO_3, HCl, and ethanol. The compositions of various microstructures were analyzed by an Oxford INCA energy-dispersive spectrometry (EDS) apparatus, with relative error of ±1%.

The phase transformation temperatures of these samples were tested by a differential thermal analysis (DTA) instrument. The specimens used for this measurement were cut from the solidified samples and were small round sheets with diameter of 5 mm and height of 1 mm. The heating and cooling rates were set at 30 K/min.

3. Results and Discussion

Figure 2 shows the as-cast microstructures of Co-20.5at.%Sn, Co-23.5.0at.%Sn, Co-24.0at.%Sn, and

Co-24.5at.%Sn. It is very clear that the microstructures of Co-20.5at.%Sn contain both primary dendritic α-phase (indicated by the arrow) and lamellar eutectic structure, as shown in Fig. 2(a). Besides, the volume fraction of the primary dendritic α-phase is quite large. It is widely known that the solidification microstructure changes considerably

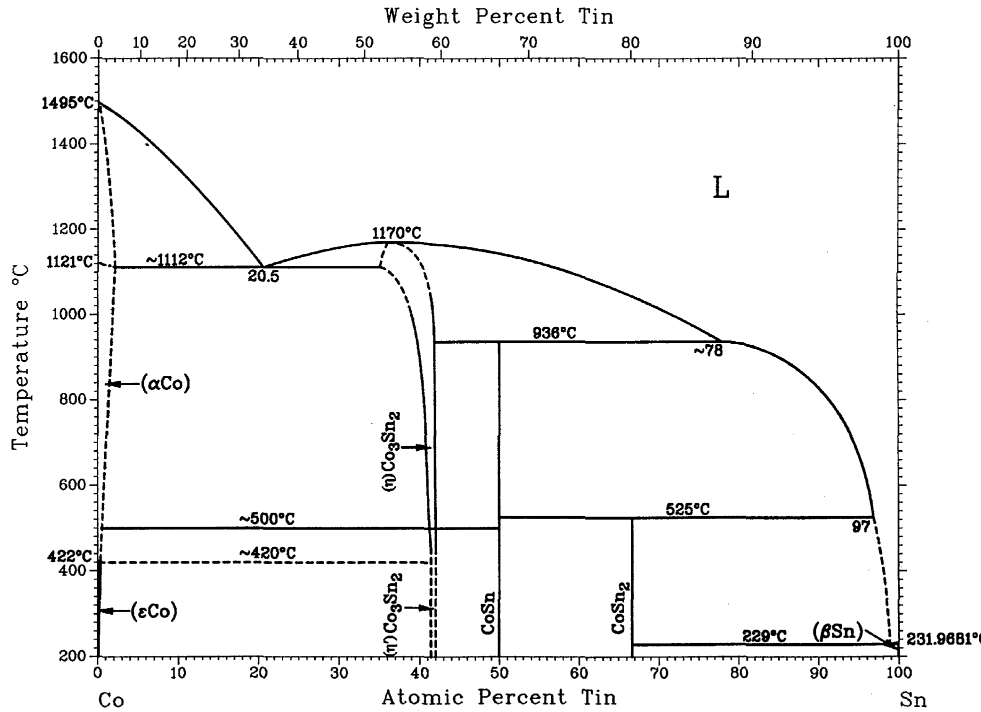

Fig. 1 Co-Sn binary alloy phase diagram[1]

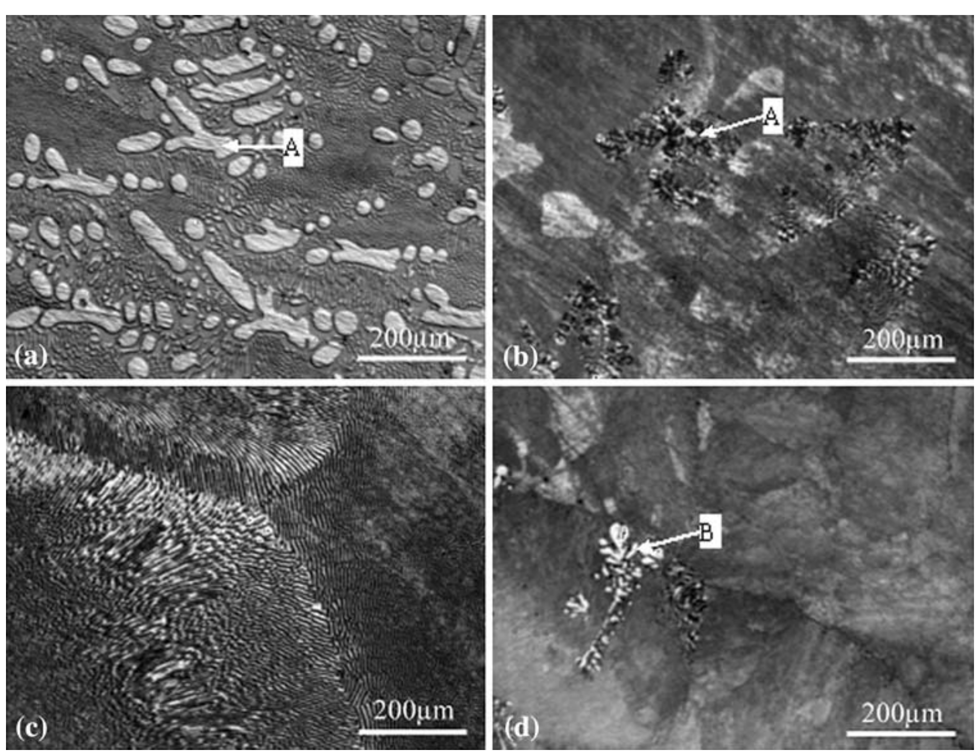

Fig. 2 The as-cast microstructures of Co-Sn alloys. (a) Co-20.5at.%Sn; (b) Co-23.5at.%Sn; (c) Co-24.0at.%Sn; (d) Co-24.5at.%Sn

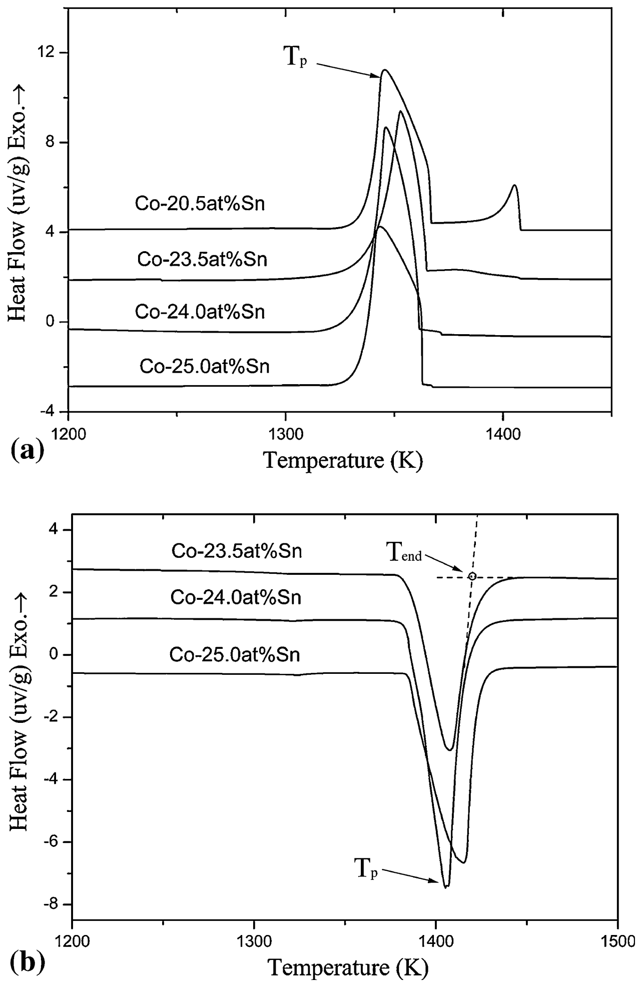

Fig. 3 DTA curves of Co-Sn alloy of different compositions. (a) Cooling curve; (b) Heating curve

with the undercooling prior to nucleation.[4-6] Therefore, during the experiment, the undercooling was controlled to not exceed 5 K. If the Co-Sn phase diagram shown in Fig. 1 were correct, i.e., Co-20.5at.%Sn is the eutectic composition, the as-cast microstructure should consist of lamellae. Even if experimental error can lead to a certain deviation from the eutectic point, it is impossible to produce so much primary dendritic phase in the microstructure. The raw materials used in the experiment were highly pure, and more than 10 specimens had been prepared to reduce the error, but similar microstructures were always obtained. Therefore, one can be sure that the eutectic composition given in the Co-Sn phase diagram is not accurate. In contrast, the as-cast microstructure of the Co-24.0at.%Sn specimen is composed of entirely lamellar eutectic, as shown in Fig. 2(c). The as-cast microstructures of Co-23.5at.%Sn and Co-24.5at.%Sn contain vast lamellar eutectic and a small amount of primary phases, marked by A and B, respectively, in Fig. 2(b) and (d). According to the energy-dispersive x-ray (EDX) analysis, the primary

Table 1 Characteristic temperatures in the DTA heating curves

Composition, at.%	Peak temperature (T_p), K	End temperature (T_{end}), K
Co-23.5Sn	1407	1428
Co-24.0Sn	1405	1422
Co-25.0Sn	1415	1427

phases marked by A and B are α(Co) phase and βCo_3Sn_2, respectively. This indicates that the compositions of Co-23.5at.%Sn and Co-24.5at.%Sn are located on the two sides of the eutectic point. The actual binary eutectic composition of Co-Sn alloy is near Co-24.0at.%Sn, and the eutectic point given in the literature[1], i.e., Co-20.5at.%Sn, is a hypoeutectic composition.

For further examination of the actual eutectic composition and temperature, DTA measurements were performed. The DTA cooling and heating curves of the specimens are shown in Fig. 3. It is very clear that two exothermic peaks exist in Co-20.5at.%Sn, and only one exothermic peak appears in Co-23.5at.%Sn, Co-24.0at.%Sn, and Co-25.0at.%Sn. The peak temperature (T_P) of Co-24.0at.%Sn is the lowest compared with those of Co-23.5at.%Sn and Co-25.0at.%Sn. Table 1 lists the characteristic temperatures on the heating curves of Co-23.5at.%Sn, Co-24.0at.%Sn, and Co-25.0at.%Sn. It shows that both the peak temperature and the melting end temperatures (T_{end}) of Co-24.0at.%Sn are the lowest. At the peak temperature, the melting rate of a specimen is the highest. The existence of primary phase increases the peak temperature of Co-23.5at.%Sn and Co-25.0at.%Sn toward higher values. The end temperature of melting sometimes is used to approximate the liquidus temperature. This means that the liquidus temperature of Co-24.0at.%Sn is the lowest among the investigated alloys. The aforementioned qualitative analyses indicate that the solidification of Co-24.0at.%Sn is composed of only a eutectic reaction. The three curves in the Fig. 3(b) exhibit the same onset temperature of melting, which is the eutectic temperature. Its average value is 1385 K (1112 °C), being consistent with the eutectic temperature shown in the Co-Sn phase diagram in Fig. 1.

4. Conclusions

The presence of primary phase in the as-cast microstructures and the two exothermic peaks in the DTA cooling curve of the Co-20.5at.%Sn alloy proves that it is not a eutectic composition. In contrast, entire lamellar eutectic microstructure is obtained in the Co-24.0at.%Sn specimen. Also, the DTA thermal analysis confirms that only one reaction happens during the solidification of Co-24.0at.%Sn. Thus, it is concluded that the actual eutectic composition is around Co-24.0at.%Sn, and the corresponding eutectic temperature is 1385 K.

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