NOTES

CHEMICAL ISOLATION OF INTERMETALLIC COMPOUNDS FROM ALUMINIUM AND ITS ALLOYS

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A chemical method for isolating second phase constituents in aluminium and its alloys is described. The matrix is dissolved in boiling phenol and the second phase is obtained as an insoluble residue. The isolation is quantitative and without effect on composition for many intermetallic compounds which are commonly present in commercial aluminium materials.

For the characterization of aluminium materials, there have been increasing demands for information on second phases in aluminium and its alloys, with respect to their type, composition, quantity, size, etc. Such demands have necessitated a technique to isolate second phase constituents, which are usually intermetallic compounds, from the matrix. Although various techniques have been reported¹⁾⁻³⁾, they were established to isolate large precipitates in experimentally prepared samples with a very high content of alloying elements. Application of these techniques to commercial materials has not been successful because of the inclusion of undissolved aluminium particles in the residue, contamination by alloying elements in solid solution, or low recovery of second phase constituents⁴⁾.

The authors discovered that the dissolution of aluminium and its alloys in heated phenol, originally reported as a method for extraction of oxide inclusions⁵⁾, resulted in several kinds of intermetallic compounds being isolated as well. The content of the oxide inclusions in the residue was negligible in most cases. For the establishment of the procedure, experiments were carried out using a series of Al-Fe-Si alloys containing a single second phase at a level equivalent to that of commercial alloys. They were prepared by casting ingots of selected compositions and heat treating under conditions appropriate for the relevant phases.

In this note, the technique and some examples of its application are described.

EXPERIMENTAL

Sample preparation

Aluminium alloy samples containing Al_3Fe , $\alpha\text{-AlFeSi}$ and $\beta\text{-AlFeSi}$ as a single second phase were prepared in the manner established by Miki⁶⁾. Ingots of an Al-0.45% Fe alloy with three levels of silicon content, namely, 0.05, 0.35 and

0.95%, were prepared by melting materials of commercial purity and casting into a permanent mould. They were subsequently heat-treated under conditions given in Table 1. X-ray diffraction and metallographic observation confirmed the absence of undesired phases.

Table 1 Samples and recovery of second phase after dissolution in heated phenol

Sample No.	Bulk content (%)		Condition of heat treatment	Second phase	Amount recovered* (%)			Recovery of second phase (%)
	Fe	Si			Al	Fe	Si	
1	0.42	0.06	600°C, 140 hr	Al ₃ Fe	0.63	0.39	0.006	93
2	0.43	0.34	620°C, 72 hr	Al ₃ Fe	0.67	0.41	0.04	95
3	0.45	0.35	490°C, 500 hr	α -AlFeSi	0.75	0.42	0.11	93
4	0.47	0.92	600°C, 140 hr	β -AlFeSi	0.96	0.45	0.23	96

* Percentage with respect to original sample weight.

Reagent and apparatus

Phenol, benzyl alcohol, methanol: Reagent grade

Membrane filter: Polytetrafluoroethylene filter with 0.8 μ m diameter pores, Type FP-080 (Sumitomo Electric Industries, Ltd.)

Dissolution apparatus: 300 ml round-bottom flask with 30 cm long Liebig-type reflux condenser and 250 W half-sphere mantle heater

Centrifuge: Model 50B-5 (Sakuma Co., Ltd.) with tube Corex 8445 CTF (Corning)

Recommended procedure of isolation

The procedure established for the isolation is as follows:

Boil 120 ml phenol in a 300 ml flask for one minute to remove water. Add 0.2 - 0.3 g sample in the phenol. Attach a reflux condenser cooled with an air flow and boil gently until the dissolution reaction ceases. Add 80 ml benzyl alcohol and cool to room temperature. Separate the residue using a centrifuge at 7,000 r.p.m. for 10 minutes. Discard the supernatant solution. Add benzyl alcohol and repeat the separation. Transfer the residue on membrane filter with methanol and filter with suction.

Analysis of isolated phases

The residue was dissolved in warm hydrochloric acid with a small addition of hydrogen peroxide. After cooling, Al, Fe and Si were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy under the following conditions:

Apparatus	:	Shimadzu Model GQM-1000P
Plasma source unit	:	ICSP-2H, 27.12 MHz, 2.5 kW
Argon flow rate	:	Coolant gas 10.5 l/min
	:	Plasma gas 1.5 l/min
	:	Carrier gas 0.95 l/min
Observation height	:	15 mm above coil
Spectral lines	:	Si 288.16 nm, Fe 259.95 nm, Al 396.15 nm

RESULTS AND DISCUSSION

Effects of experimental variables

The procedure described in the previous chapter is essentially the same as that reported by Kiba et al.⁵⁾, except the use of a centrifuge and membrane filter. Filtration with ordinary filter paper is not efficient due to the high viscosity of the solution. As for the rate of centrifuging, 7,000 r.p.m. was chosen because the recovery levelled off at rates higher than 5,500 r.p.m. At 4,500 r.p.m., the recovery dropped to 70%. Pore size of the membrane filter did not affect the recovery in the range between 0.2 and 0.8 μ m.

Contamination of the residue by aluminium-bearing precipitates, probably aluminium phenolate, was observed to take place when 0.4 g sample was dissolved in 120 ml phenol. From the result of an experiment, 0.3 g was chosen as the maximum quantity of a sample for 120 ml phenol.

Recovery of second phase constituents

Since the solid solubility of iron in aluminium is very low, the element should be present as a second phase, while excess silicon (surplus for relevant phase formation with Fe and Al) should be in solid solution in the matrix. Therefore, the recovery of the second phase was assessed from that of Fe. As shown in Table 1, the recovery exceeded 90% for all samples. The composition of the phase recovered agreed quite well with that reported in the literature, as shown in Table 2.

From these results, it is concluded that this method is capable of isolating Al-Fe-Si phases quantitatively without affecting their composition.

Table 2 Composition of residue isolated by dissolution in heated phenol

Sample No.	Phase	Content in residue (%)		Content in the phase reported in literature (%)		Reference
		Fe	Si	Fe	Si	
1	Al ₃ Fe	38	<1			
2	Al ₃ Fe	37	3	38.9	-	7)
3	α -AlFeSi	33	9	32.5	8.5 - 10.5	1)
4	β -AlFeSi	27	14	27	13.8 - 15	1)

It is of interest that the Al₃Fe phase in sample No. 2 contained some silicon, although its X-ray diffraction pattern was same as that of sample No. 1. The silicon in this phase might change its characteristics, for example, response to chemical treatment.

Application to commercial alloys

The isolation technique was applied to variety of commercial aluminium alloys (JIS H4100) and the extracted phases were examined by X-ray diffraction. The phases listed below were found in the residue, either singly or as a mixture. The absence of intense diffraction due to the aluminium matrix enabled the detection of minor phases.

1000 series (commercial purity Al):	Al_3Fe , Al_6Fe , Al_mFe , $\alpha\text{-AlFeSi}$
2000 series (Al-Cu system alloys):	Al_2Cu , $\alpha\text{-AlFeMSi}^*$, $\text{Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6$
3000 series (Al-Mn system alloys):	$\text{Al}_6(\text{Mn}, \text{Fe})$, $\alpha\text{-AlFeMnSi}$
4000 series (Al-Si system alloys):	Si , $\beta\text{-AlFeSi}$
5000 series (Al-Mg system alloys):	Mg_2Si , $\alpha\text{-AlFeMSi}^*$, Al_3Fe
6000 series (Al-Mg-Si system alloys):	Mg_2Si , $\alpha\text{-AlFeMSi}^*$, $\beta\text{-AlFeSi}$
7000 series (Al-Zn-Mg system alloys):	MgZn_2 , Al_2CuMg , Mg_2Si
* M denotes various transition metal elements.	

Al_mFe is a metastable phase with body centered tetragonal structure and the value of m has been reported as 4.4, by EDX analysis⁸). The Al_mFe phase was isolated singly from a 1000 series alloy using the present technique. The value of m , which was determined by chemical analysis, was also found to be 4.4.

In Al-Mg-Si system alloys, two types of Mg_2Si phase are present, namely, relatively large precipitates formed during solidification and very fine precipitates formed during artificial ageing. It was found that this technique isolated the former only, probably due to the small size of the latter. Therefore, distinguishing Mg_2Si of the both types is possible, which should give very useful information for the characterization of the alloys of this system.

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