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ALUMINIUM-BASED DILUTE ALLOYS OBTAINED IN A PLASMA FURNACE AND CONTROLLED BY ACTIVATION ANALYSIS

A.A.Samadi*, R.Grynszpan, M.Fedoroff

Centre d'Etudes de Chimie Métallurgique, 94400 Vitry, France

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Homogeneous aluminium-based alloys containing Cu, Mn, Pd, Pt, Ir, Ru or Os in the 0.5 to 20 000 µg/g range have been obtained by melting in a plasma furnace. Concentrations were determined by neutron activation analysis. This method achieved the accuracy range of 1 %, as it was shown by comparison with the expected values and with those obtained by double irradiation technique and atomic absorption spectrometry.

INTRODUCTION

Dilute alloys have an increasing importance in solid state physics and in analytical chemistry. The properties of metals are strongly affected by low concentrations of impurities[1]. The most effective method to understand the effect of a given impurity is to use dilute alloys with well known concentrations of the foreign element.

There is also an increasing need of standard dilute alloys in all trace-analysis methods. In activation analysis, the concentrations are determined either by using a standard for each investigated element or by using a flux monitor. The choice of

* Visiting scientist from Mashed University, Iran

standards or monitors is subjected to the following conditions: well-known quantity of the element, stability during irradiation, counting geometry identical to that of the sample, induced radioactivity of the same order of magnitude, no error due to interference or self-absorption produced by the matrix elements. These conditions are not easily fulfilled simultaneously.

The method of preparing standards by depositing a given volume of a solution on a substrate cannot be used if the element /as e.g. Ir, Ru and Os/ or one of its stoichiometric compounds is not easily dissolved in a reagent suitable for further irradiation. Furthermore, the fluxes and temperature occuring in the reactors often lead to a decomposition of either the substrate or the compound of the standard element.

Unfortunately alloys with the concentrations required to obtain the desired radioactivity after irradiation are not commercially available. Alloys of some elements are not available at all. For this purpose, i.e. for the studies of the physical properties of metals, one would need alloys with concentrations from 0.1 ppm to 1 %.

EXPERIMENTAL

Materials

Aluminium was chosen as the matrix metal owing to the purity available in our laboratory /zone refined Al: 99.9999 %/[2], the metallurgical studies undertaken on its solid solutions in copper[3], and the nuclear properties of this matrix.

Doping elements were: Cu /99.999 %/ produced by the A.S.A.R. Co, electrolytically purified Mn /99.99 %/ provided by the Pro-

labo,Pd /99.99 %/, Pt /99.999 %/, Ir /99.99 %/, Ru /99.9 %/, and Os /99.97 %/ provided by the Koch Light Laboratories.

Plasma furnace melting

Among the methods of alloying aluminium, the melting in an induction plasma furnace[4] was chosen for its following main advantages: speed of performance, melting at very high temperature /possibility of using refractory doping elements as Os/, good mixing due to the high-frequency currents, favourable atmosphere avoiding oxidation, limited pollution, and quenching without casting.

To obtain an alloy with a given content, pieces of aluminium and those of the solute metal were weighed with an electric balance with an accuracy of 5 μg. The foreign metal was set rapidly into a hole of the matrix. Melting in the furnace was performed on a water cooled cupper crucible. Plasma was induced in a hydrogen-argon flow. In order to remove the dissolved hydrogen gas from the material, successive meltings /30 sec each/ of the obtained button were carried out under pure argon plasma. Absence of gaseous inclusions have been tested by observations under microscope.

Further metallurgical treatments as cold-work and vacuum annealings /12 hrs at 500°C/ were performed on the samples used for the investigation of the physical properties.

Highly dilute alloys were prepared by dissolving the most concentrated alloys in pure aluminium. Successive dilutions lead to the lowest concentrations prepared /0.5 ppm/.

Conventional activation analysis

To determine the concentration and the homogeneity of the alloys, a diametric slice of each spherical button was taken and cut into 10 pieces of 10 to 30 mg. The samples were irradiated by thermal neutrons in the EL3 reactor /Saclay, France/, with fluxes of some 10^{12} cm^{-2} sec^{-1}. The duration of irradiation varied from 10 min to several days, according to the concentration to the half-life and cross section of the investigated element. A given weight of the pure element and, when possible, a known quantity deposited on a filter paper from a solution were irradiated simultaneously as standards. Countings were performed by NaI/Tl/ and Ge/Li/ detectors coupled to height pulse analysers[5] on samples and standards in solid phase and after dissolution. Volumes of solutions were adjusted with a 0.1 % accuracy. In most cases, the standard deviation in counting statistics was less than 1 %.

Double irradiation technique

The double irradiation technique eliminates the sources of errors due to interferences which might come from the irradiated matrix. The alloys was made from non radioactive aluminium and from an irradiated piece of the doping element. After alloying, weighed pieces of the material /about 100 mg/ were dissolved in aqueous solution and the radioactivity measured on an liquot. The concentration was deduced from the radioactivity of an aliquot of the solution of another piece of the doping metal, simultaneously irradiated. After the decay of the radioactivity, the alloy was irradiated for conventional activation analysis.

Atomic absorption spectrometry

For copper determination, alloys of the pure metal were dissolved in order to obtain aqueous solutions of about 3 mg/l of Cu. Aluminium concentration was ajusted to a constant value. Atomic absorption was measured at 0.3247 μm wave length by a Jobin-Yvon spectrophotometer.

RESULTS AND DISCUSSION

Homogeneity

Table 1 gives the mean value and the estimated standard deviation of the concentration calculated for 4 to 12 samples. This relative standard deviation is less than 3 % except for the most concentrated alloys of Os and Ru. In the case of the Mn and Cu alloys, the standard deviation is less than 1 %.

Accuracy

We had several means of testing the accuracy of the determinations. One of these is the comparison between the concentrations expected and found. The agreement is good /generally less than 3 % deviation/ for all dilute alloys. The agreement is poorer for the most concentrated alloys /above 0.1 %/ of high melting point metals /Ir, Ru and Os/.

The results obtained by both irradiations and by NaI/Tl/ and Ge/Li/ counting in liquid phases are in good agreement /Table 2/. On the other hand, the solid phase countings give slightly different values, probably due to differences in geometry and radiation absorption.

The relative deviation between activation analysis and atomic absorption results is less than 1.2 % for Al-Cu alloys of 2.56 % and 1.95 % Cu.

TABLE 1

Activation analysis of aluminium-based alloys

Doping element /melting point/	Expected concentration µg/g	Observed mean concentration µg/g	Relative deviation from the expected concentration %	Relative standard deviation /homogeneity/ % **
Cu /1083°C/	1382	1377	-0.4	0.6
Mn /1245°C/	426	427	+0.2	0.7
Pd /1552°C/	3820 3200	4030 3330	+5.5 +4.1	2.8 2.7
Pt /1769°C/	3650	3720	+1.9	1.6
Ir /2454°C/	4205 50.0 33.7 5.00 0.500	3914 50.5 * 33.2 * 5.16* 0.506*	-6.9 +1.0 -1.5 +3.2 +1.2	1.4 1.8 2.7 2.3 2.6
Ru /2500°C/	4300 50.0	3384 45.6 *	-21.3 - 8.8	3.3 2.2
Os /3000°C/	17390 6190 50.2 5.00	20133 6780 50.45* 4.98*	+15.8 + 9.5 + 0.5 - 0.4	5.5 1.3 2.0 2.4

* alloys prepared by successive dilutions
** deduced from determinations on 4 to 12 samples

TABLE 2

Mn concentration µg/g/ of an Al-Mn alloy determined by various activation analysis procedures

Expected concentration	First irradiation NaI detector /liquide phase/	Second irradiation		
		liquid phase		solid phase
		NaI	Ge/Li/	Ge/Li/
426	424 ± 3	426 ± 3	430 ± 4	404 ± 4

CONCLUSION

Melting in a plasma furnace is a quick and reliable method of making homogeneous dilute aluminium-based alloys. With this method, we were able to produce alloys with concentration quite near the expected values, which are as low as 0.5 ppm in some cases. We also had the opportunity of controlling the accuracy of activation analysis which can easily achieve the 1 % range.

We now use these dilute alloys as standards in activation analysis and for the study of the radiochemical separation of an impurity in the real conditions of a dissolved sample[6]. Other applications are studies on physical properties of aluminium.

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