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FAST NEUTRON ACTIVATION ANALYSIS OF SILICON IN ALUMINUM ALLOYS

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The silicon content in an aluminum – silicon alloy was measured by nondestructive fast neutron activation analysis with fission spectrum neutrons. A boron nitride irradiation container reduced the flux of thermal and epithermal neutrons at the sample position, enhancing the ^{29}Si (n, p) ^{29}Al reaction. A detection limit of 0.4% silicon in a 0.5 g alloy sample was obtained.

Introduction

The automotive applications of aluminum-silicon alloys include cylinder heads, pistons, valve bodies, fuel pump bodies, crankcases, transmission cases, axle housings, and wheels.[1] In the majority of these applications, the silicon content ranges from 5 to 13%, with differences in the silicon content and other constituent elements determining the final use of the alloy. Assay of the silicon content in these alloys is required when testing prototypes.

The ASTM standard methods for assay of silicon in aluminum and aluminum-based alloys are photometric and gravimetric procedures.[2] Silicon in the 0.05 to 20.0% range is determined either by the molybdisilicic acid (photometric) method or by the sodium hydroxide – perchloric acid (gravimetric) method. Both methods involve tedious and time-consuming chemical treatment of the sample whereby errors arising from reagent contamination, incomplete sample dissolution, and loss of silicon by spattering may occur.

The determination of silicon in aluminum alloys by instrumental neutron activation analysis (INAA) eliminates these problems since no sample dissolution or pretreatment is necessary. Neutron activation analysis of silicon in a variety of matrices has been reported for the fast neutron reaction ^{28}Si(n, p) ^{28}Al using 14 MeV neutrons from a neutron generator.[3,4] Fission reactors provide fluxes of fast neutrons comparable to 14-MeV neutron (DT) generators, and ÖRDÖGH et al.[5] have

demonstrated an assay based on activation of silicon in biological materials with fission spectrum neutrons. They used the ^{28}Si (n, p) ^{28}Al reaction, minimized the ^{27}Al (n, γ) ^{28}Al contribution by shielding the sample in cadmium metal, and corrected for ^{31}P (n, α) ^{28}Al by means of a colorimetric method for phosphorus. Subsequently JONES et al.[6] made similar assays, but added the ^{29}Si (n, p) ^{29}Al reaction as a second determination when silicon levels exceeded 0.5%.

Experimental

An assembly of a polyethylene sample container, a boron nitride neutron filter, and associated polystyrene cushions in a polyethylene rabbit was devised for irradiating samples in the pneumatic tube system at the Ford Nuclear Reactor at the University of Michigan. Boron nitride was selected as the slow neutron absorber because of its high neutron attenuation (due to ^{10}B), machinability, relative absence of induced radioactivity, and tolerance of high temperatures. In our design the 1.07 $g \cdot cm^{-2}$ areal density of the BN wall gives an effective neutron cutoff of 62 eV.[7]

High purity silicon chips served as standards. As a cross check, we used a standard reference material (SRM 87a) from the U. S. National Bureau of Standards. This material contains 6.24% silicon. In order to test the method on a practical sample, duplicate samples from an aluminum silicon alloy automotive part were analyzed for silicon content.

Individual samples (0.5 g except 0.05 g for Si chips used as standards) were packaged and irradiated for 5 min in the boron nitride capsule. The fast neutron flux was measured by irradiating an aluminum foil and counting the induced ^{24}Na activity ($\Phi fast = 6.8 \cdot 10^{11}$ $n \cdot cm^{-2} \cdot s^{-1}$, $\Phi(E_S^{eff})_{8.15MeV} = 3.4 \cdot 10^9$ $n \cdot cm^{-2} \cdot s^{-1}$). Experience has shown that aluminum foils can be irradiated simultaneously with the sample; however, the small variations in neutron flux observed did not warrant continuous monitoring of each sample. Gamma-ray spectra were collected for 20 min following a 15 min cooling period (allowing decay of the 2.3 min half-life ^{28}Al activity) with a coaxial lithium-drifted germanium detector (Canberra Industries, 21 percent efficiency relative to ^{60}Co) and a Nuclear Data 6660, operated as a 4096-channel analyzer system. The Nuclear Data 6660 multiplet analysis program was used for data reduction.

A significant aspect of the present method is its relative simplicity. With 2 keV resolution and the 0.5 keV/channel dispersion of our procedure, the 1268 and 1273 keV peaks could be reliably resolved by the multiplet program. (In most cases this program was superior to treating the 1273 line as an isolated peak.) JONES et al.[6] grouped the 1268 and 1273 peaks, and corrected for the 1268 contribution by an empirical factor applied to the area of the 1779-keV full energy peak of ^{28}Al.

Results and discussion

Products of neutron activation of silicon and aluminum (and other elements likely to be present in aluminum alloys) are given in Table 1.[3,8-12] The spectral features of ^{28}Al and ^{29}Al are given in Table 2.[11] Our choice of the ^{29}Si (n, p) ^{29}Al reaction is based on the following considerations. The ^{30}Si (n, p) ^{30}Al reaction is inappropriate because of the short half-life of ^{30}Al. The ^{27}Al (n, α) ^{24}Na reaction interferes with the ^{30}Si (n, γ) ^{31}Si reaction, as explained below. Finally, the product of the ^{28}Si (n, p) ^{28}Al reaction is the same as the product of neutron capture in the bulk material, ^{27}Al (n, γ) ^{28}Al. This capture reaction is much less pronounced with fast neutrons from a DT generator, for which carefully designed irradiation geometries can provide insignificant fluxes of low energy neutrons (i. e., neutrons with large capture probabilities).

Table 1
Relevant reactions for 14 MeV and thermal neutrons

Reaction	Abund. %	$\sigma_{14\,MeV}$ or thermal, mb	E_T, MeV	σ, mb	E_{eff}, MeV	σ_o, mb	Half-life	Gamma energy, MeV
^{28}Si(n, p) ^{28}Al	92.2	250	4.01	4.0			2.3 m	1.78(100%)
^{29}Si(n, p) ^{29}Al	4.7	100	3.1	2.7			6.52 m	1.28(91%)
^{30}Si(n, p) ^{30}Al	3.1	60					0.05 m	2.23(61%)
^{30}Si(n, γ) ^{31}Si	3.1	110_{th}					2.6 h	1.27(. 07%)
^{27}Al(n, γ) ^{28}Al	100	231_{th}					2.3 m	1.78(100%)
^{27}Al(n, α) ^{24}Na	100	118	3.27	0.6	8.15	120	15 h	2.75(99%)
^{31}P(n, p) ^{31}Si	100	82	0.72	31.2	3.0	140	2.6 h	1.27(. 07%)
^{31}P(n, α) ^{28}Al	100	150	2.02	1.4			2.3 m	1.78(100%)
^{23}Na(n, p) ^{23}Ne	100	40	3.76	0.7			38 s	0.44(32%)
^{23}Na(n, γ) ^{24}Na	100	930_{th}					15 h	2.75(99%)
^{24}Mg(n, p) ^{24}Na	79.0		4.95	1.3	8.00	200	15 h	2.75(99%)
^{26}Mg(n, α) ^{23}Ne	11	85					38 s	0.44(32%)
^{26}Mg(n,γ) ^{27}Mg	11	38_{th}					9.5 m	0.84(72%)

Table 2
^{28}Al and ^{29}Al gamma radiation

Isotope	Gamma energy, MeV
^{28}Al	0.7568 Pair peak
^{28}Al	1.2678 Pair peak
^{28}Al	1.7788 100.0A
^{29}Al	1.2730 91.0A
^{29}Al	1.4040 Pair peak
^{29}Al	1.9150 Pair peak
^{29}Al	2.0280 3.4 A
^{29}Al	2.4260 5.5A

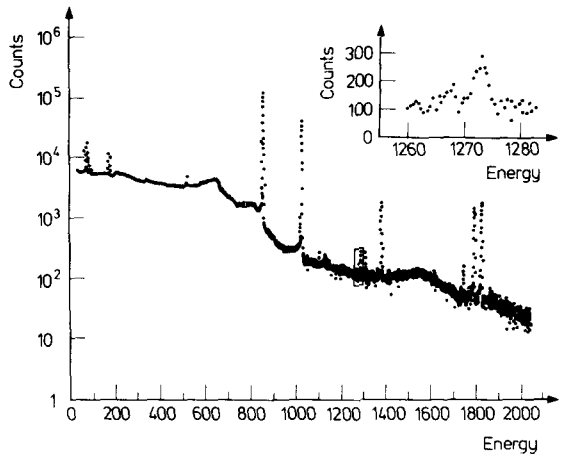

Fig. 1. Spectrum of NBS SRM 87a. Enlarged detail shows distribution of 1268 and 1273 keV gamma-rays

In principle one might expect the best detection of Si in Al from the ^{30}Si (n, γ) ^{31}Si reaction. Although the abundance of the 1.27-MeV gamma-ray is low, activation can be carried out for several hours, and decay times can be long enough to insure complete decay of ^{28}Al. However, unless the irradiation position corresponds to an extremely well-thermalized flux (an unusual condition in small research reactors), fast neutrons will produce such large amounts of ^{24}Na from the aluminum that detector systems cannot accommodate samples of many milligrams. In fact, this production of ^{24}Na is a major limiting factor in the irradiation time for our experiments.

The timing of the several steps in the procedure involves a compromise among allowing sufficient time for ^{28}Al to decay relative to ^{29}Al, preventing the ^{29}Al/^{24}Na ratio from becoming too low, and counting for a long enough time to obtain adequate statistics. The nature of this compromise can be seen from the data (see Fig. 1) obtained for an aluminum alloy containing 6% Si. Times for irradiation, cooling, and counting were 5, 15, and 20 min, respectively. The irradiation period might have been chosen as 6.5 min as the best balance between saturation of ^{28}Al and maintaining a high ratio of ^{29}Al/^{24}Na, but 5 min is more convenient because beyond that time polyethylene is likely to soften too much (from heating of the capsule from the ^{10}B (n, α) ^{7}Li reaction).

The 15-min cooling time seems optimum for a typical sample in the 0.5 to 15% Si range. For the 20 min count the net area of the peak (900 counts) and the background due to ^{24}Na (1200 counts) are approximately equal. For lower Si content shorter counting times would be better (improved signal to noise ratio for ^{29}Al vs. ^{24}Na), but for higher Si contents longer times give marginally better statistical accuracy. The times specified are optimized for alloys of 10% Si in Al.

Table 3
Results

Sample	Counts per 1200 s*	Sample, mg	Silicon, mg	Counts per 1200 s per mg Si	% Si calculated**
Si chip	1972±53	53.22	53.22	37.05±1.00	
Si chip	1834±54	50.12	50.12	36.59±1.08	
SRM 87a	1190±74	507.98	31.70	37.54±2.33	6.36±0.40
SRM 87a	1097±72	502.17	31.34	35.00±1.96	5.93±0.39
Unknown	3221±95	541.76			16.15±0.48
Unknown	2712±90	501.24			14.69±0.49

*Corrected for dead time.
**Based on 36.82 counts per 1200 s per mg Si.

Larger samples (up to 5 g) can be accommodated in the irradiation capsule without encountering problems with flux attenuation of the energetic neutrons (~ 8 MeV) responsible for the reaction. However, the detector/analyzer system operates at 15 to 25% dead time with 0.5 g samples, and this is a practical limit for reliable count rate corrections.

Standardization data and test results are given in Table 3. The dominant uncertainty in the assays derives from counting statistics. The standards do not present count rate limitations due to ^{24}Na, and the correlation between the amount of Si and the count rate for 1273-keV gamma-rays can be established with a statistical accuracy much better than necessary for samples. The reference material (NBS SRM 87a) is known to be uniform, and the duplicate Si determinations, each with a statistical uncertainty of 1 σ = 6.5%, differ from the known Si content by less than 5%. The unknowns are portions of the same part; it is not certain that the part is homogeneous with respect to Si. Although the difference between the results is larger than those observed for the standards and references, the difference is consistent with statistics due to counting. The 2 σ detection limit calculated for the alloy sample is 0.4% Si in a 500 mg sample. This limit corresponds to that found by BUCZKO et al.[2] for Si assay with a DT generator.

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