Prevention of Ge Volatilization in the Chemical Treatment of Ge-Cr-Al-Ce-Sm Amorphous Alloy for the Determination of Ge by ICP-AES

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Introduction

For the dissolution procedure of Ge alloys, several mixtures of acids have been investigated: HNO_3 -HF,¹⁻⁴ H_2SO_4 - HNO_3 -HF,^{5,6} and HNO_3 -tartaric acid.⁷ However, such acid mixtures cannot be applied to the dissolution of Ge alloys containing Cr, due to a Cr stable oxide film hindering the reaction; therefore, a mixed acid containing large amounts of HCl should be employed for the dissolution. On the other hand, it has been reported that Ge easily volatilizes as GeCl_4 when using aqua regia as the dissolvent.² One must pay careful attention to the volatilization loss of Ge. Another study revealed that metallic Ge could be completely dissolved without any volatilization loss by using a mixed acid of 35 ml of HNO_3 (diluted 1 + 1), 5 ml of HCl (diluted 1 + 1), and 1 g of tartaric acid as a dissolvent.⁸ However, this method is not also applied to the dissolution of Ge alloys containing Cr, because Ge begins to volatilize when the concentration of HCl in the mixed acid increases.⁸

In this paper, we report on a new method for the pretreatment of Ge alloys with no volatilization loss of Ge, even with a mixed acid containing much HCl. This developed method can be applied to the analysis of a Ge-Cr-Al-Ce-Sm amorphous alloy by ICP-AES.

Experimental

Apparatus, reagents and solutions

The employed Hitachi P-5200 system and its operating conditions are given in Table 1. The analytical spectral lines were determined by using a program for line selection that we have developed.^{9,10}

Standard reagents with purities of 99.9 to 99.999% and chemicals of analytical-reagent grade were used.

Acid mixture: 400 ml of H_3PO_4 (diluted 1 + 1), 400 ml of H_2SO_4 (diluted 1 + 1), 200 ml of HNO_3 , 200 ml of HCl, 400 ml of HF, and 400 ml of water were mixed.

Ce standard solution (0.600 g/l): 73.70 mg of CeO_2 that was weighed after heating in a platinum crucible was dissolved with 10 ml of HNO_3 (diluted 1 + 1) and 5 ml of H_2O_2 ; then, 10 ml of HCl (diluted 1 + 1) was added, and finally diluted to exactly 100 ml after complete decomposition of H_2O_2 by heating.

Sm (0.400 g/l), Al (0.200 g/l), and Cr (0.700 g/l) standard solutions: the required amount of Sm_2O_3 that was made constant weight in the same manner as CeO_2 ; then, metallic Al and metallic Cr were dissolved in 10 ml of HCl (diluted 1 + 1), and

finally diluted to exactly 100 ml, respectively.

Zn solution (5 g/l): 5 g of metallic Zn was dissolved with 50 ml of HNO_3 (diluted 1 + 1), and then diluted to 1000 ml with water.

Prevention of Ge volatilization

When a Ge solution is prepared with a mixed acid containing small amounts of HCl and no HF, it is generally observed that Ge is volatilized in the development of fuming H_2SO_4 - H_3PO_4 . The loss of Ge would be more serious if a mixed acid containing more HCl is required to dissolve alloys containing a large amount of Cr. In order to prevent such volatilization of Ge, even in the co-presence of a mixed acid having high HCl concentration, we developed the following procedure.

Metallic Ge of 100 mg placed in a PTFE beaker was dissolved in a mixed acid comprising 10 ml of H_2SO_4 : H_3PO_4 : H_2O (1:1:2), 0 to 15 ml of HF, 5 ml of HNO_3 , and 15 ml of HCl. Moreover, a reference solution without HCl was prepared by using metallic Ge of 110 mg, and a mixed acid comprising 10 ml of H_2SO_4 : H_3PO_4 : H_2O (1:1:2), 2 ml of HF, and 10 ml of HNO_3 (diluted 1 + 1). The inside of the beaker was washed with a few ml of water after concentrating the solutions to almost fuming H_2SO_4 - H_3PO_4 on a hot plate. The solutions were concentrated in the fuming operation for 5 min. The resulting salts were dissolved in about 30 ml of water with heating. The solution was diluted to 100 ml after adding a Zn solution (5 g/l) of 10 ml as an internal standard for ICP-AES. The final solutions were determined by ICP-AES. To obtain results on Ge recovery, Ge solutions containing various amounts of HCl (from 10 to 39 ml) were also prepared.

Analysis of Ge-Cr-Al-Ce-Sm amorphous alloy

A sample of 60 mg placed in a PTFE beaker was dissolved with 25 ml of the acid mixture (the same composition as that for the Ge dissolution) taken with a polypropylene pipette. The inside of the beaker was washed with a few milliliters of water after concentrating the solution to almost fuming H_2SO_4 - H_3PO_4 on a hot plate. The solution was concentrated while keeping the fumes of H_2SO_4 - H_3PO_4 for 5 min. The salts were dissolved in about 30 ml of water by heating. A Zn solution (5 g/l) of 10 ml was added as an internal standard for ICP-AES; finally, the solution was diluted to 100 ml. To determine the calibration curves of the constituent, solutions containing each element were individually prepared with standard solutions of each element and metallic Ge by the same dissolution method as the sample solution, with the exception that 10 ml of HNO_3 was added to 25 ml of the acid mixture due to rapid dissolution of metallic Ge.

Table 1 Instrument and operating conditions

ICP source		Hitachi P-5200 ICP emission analysis system	
Plasma operating power		1.0 kW	
Frequency		27.12 MHz	
Argon flow rates			
Outer gas		12 l/min	
Intermediate gas		0.5 l/min	
Carrier gas		0.5 l/min	
Spectrometer		Vertical dualmonochromator	
Type		Czerny-Turner type	
Mounting		750 mm	
Focal distance			
		Spectrometer 1	Spectrometer 2
Grating		3600 grooves/mm	1200 grooves/mm
Slit width		30 μm	30 μm
Slit height		10 mm	10 mm
Reciprocal linear dispersion (1st order)		0.29 nm/mm	1.06 nm/mm
Observation height		15 mm above load coil	
Optical path		in air	
Photomultiplier voltage		350 – 750 V	
Fixed-wavelength mode		integration time: 3 s × 3-times	
Spectral line used (nm)			
(Spectrometer 1: measured element lines; Spectrometer 2: internal standard line)			
Al I 396.152	Cr II 276.654	Ge I 265.118	Ce II 413.380
Sm II 359.260	Zn I 213.856 (internal line)

Fig. 1 Recovery of Ge when concentrated to fuming after the dissolution of metallic Ge (100 mg) with a mixed acid of 10 ml of $\text{H}_2\text{SO}_4\text{:H}_3\text{PO}_4\text{:H}_2\text{O}$ (1:1:2), 0 to 15 ml of HF, 5 ml of HNO_3 and 15 ml of HCl.

Fig. 2 Influences by HCl on the recovery of Ge when concentrated to fuming after dissolution of metallic Ge (100 mg) with a mixed acid of 10 ml of $\text{H}_2\text{SO}_4\text{:H}_3\text{PO}_4\text{:H}_2\text{O}$ (1:1:2), 2 or 10 ml of HF, 1 to 30 ml of HNO_3 , 39 to 10 ml of HCl and 0 or 40 ml of water.

Results and Discussion

Prevention of Ge volatilization

Ge dissolved in $\text{HNO}_3\text{--HCl}$ solutions having high HCl concentration would volatilize as GeCl_4 , and Ge dissolved in $\text{HNO}_3\text{--HF}$ solutions would volatilize partly as GeF_4 with the progress of concentrating or evaporating to dryness. By concentrating a $\text{H}_2\text{SO}_4\text{--HNO}_3\text{--HF}$ solution of Ge (more than a few mg) to the fume of H_2SO_4 , rutile-type GeO_2 was formed, which caused a troublesome problem because it could not be dissolved in heated water, but could be dissolved easily in HF.⁶ It was found by a preliminary experiment that the rutile-type GeO_2 was not produced by using $\text{H}_2\text{SO}_4\text{--H}_3\text{PO}_4$ instead of H_2SO_4 alone. From these results, we considered the dissolution procedure of metallic Ge. Figure 1 shows the recovery of Ge

when 100 mg of metallic Ge was dissolved in a mixed acid consisting of 10 ml of $\text{H}_2\text{SO}_4\text{:H}_3\text{PO}_4\text{:H}_2\text{O}$ (1:1:2), 0 to 15 ml of HF, 5 ml of HNO_3 , and 15 ml of HCl, and then concentrated up to the fume of $\text{H}_2\text{SO}_4\text{--H}_3\text{PO}_4$. Ge was not volatilized in the co-presence of 1 to 15 ml of HF for 100 mg of Ge. Figure 2 shows the recovery of Ge when 100 mg of metallic Ge was dissolved in mixed acids consisting of 10 ml of $\text{H}_2\text{SO}_4\text{:H}_3\text{PO}_4\text{:H}_2\text{O}$ (1:1:2), 2 or 10 ml of HF, 1 to 30 ml of HNO_3 , 10 to 39 ml of HCl, and 0 or 40 ml of water, and then concentrated up to the fume of $\text{H}_2\text{SO}_4\text{--H}_3\text{PO}_4$. We could find the concentration ranges of HF as well as HCl to restrain the volatilization loss of Ge. In the presence of 2 ml of HF, little loss of Ge was observed in 0 to 37 ml of HCl. These effects were probably because of $[\text{GeF}_6]^{2-}$ being more stable than $[\text{GeCl}_6]^{2-}$ or GeCl_4 in aqueous solution.

Table 2 Analytical results for a Ge amorphous alloy and synthesized solutions

Sample	Analytical results: wt-% for an alloy ($n = 4$, average value $\pm$ standard deviation), and mg for mixed solutions ($n = 1$) ^a					
	Ge	Cr	Al	Ce	Sm	Total
Ge amorphous alloy	69.43 $\pm$ 0.22	9.988 $\pm$ 0.025	3.468 $\pm$ 0.009	9.748 $\pm$ 0.079	7.601 $\pm$ 0.030	100.23 $\pm$ 0.20
Synthesized solution A	47.01 [47.17]	5.637 [5.635]	1.106 [1.098]	4.027 [4.075]	3.557 [3.566]	61.34 [61.54]
Synthesized solution B	46.90 [47.14]	4.213 [4.226]	1.552 [1.537]	5.503 [5.433]	2.663 [2.675]	60.83 [61.01]

a. The numerical values in square brackets: quantities of elements taken in mixed solutions.

Consequently, the co-presence of HF enabled metallic Ge to be dissolved without any Ge loss, even by using a mixed acid having a high HCl concentration.

Analytical results of Ge-Cr-Al-Ce-Sm amorphous alloy

The alloy was not able to dissolve perfectly by using either a mixed acid of 40 ml of HNO₃ (diluted 1 + 1) and 1 g of tartaric acid,⁷ or a mixed acid of 35 ml of HNO₃ (diluted 1 + 1), 5 ml of HCl (diluted 1+1), and 1 g of tartaric acid.⁸ The dissolution method developed for metallic Ge was successfully applied to a treatment of the alloy. The analytical results are shown in Table 2. Synthesized solutions A and B were prepared by adding Ce, Sm, Al, and Cr standard solutions to the solution where metallic Ge was dissolved with 25 ml of the acid mixture and 10 ml of HNO₃, and treated in the same way as the sample after fuming H₂SO₄-H₃PO₄. Rare earth elements were precipitated as fluorides in a mixed acid containing HF, but fuming H₂SO₄-H₃PO₄ could dissolve them. Based on the analytical results for each synthesized solution, the accuracy for the analysis was satisfactorily confirmed. Calibration relations were estimated using individual element solutions because the matrix matching was difficult to be employed in a routine analysis due to spectral and non-spectral interferences.¹¹ Good results were obtained by the sequential correction method,¹² which consists of corrections of the fluctuation in the emission intensities, impurities in the standard reagents, spectral interferences, non-spectral interferences, and blank values.

Conclusions

The dissolution method for Ge suggested in this study has advantageous features: no volatilization loss of Ge and no

formation of rutile-type GeO₂. The addition of HF is fairly effective for preventing Ge loss as GeCl₄ in the co-presence of large amounts of HCl, since HF works to make a more, stable complex of Ge in an aqueous solution. This method allows to use of HCl, and therefore could be applied to the dissolution of Ge alloys containing Cr. The analytical results of the Ge-Cr-Al-Ce-Sm amorphous alloy could be obtained by ICP-AES.

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