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Elastic moduli of the Laves-phase pseudobinary compounds $Zr(Al_xFe_{1-x})_2$ as determined by ultrasonic measurements

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Ultrasonic methods have been used to measure the polycrystalline elastic moduli of the Laves-phase pseudobinary compounds $Zr(Al_xFe_{1-x})_2$ for $0.04 \le x \le 1.0$. The bulk modulus decreases with increasing x up to the change from cubic ($C15$) to hexagonal ($C14$) structure at $x=0.25$. The shear modulus is essentially constant in the cubic phase. At the phase boundary the bulk modulus is about 6% higher in the hexagonal phase than in the cubic phase, while the shear modulus is the same in the two phases. As x increases in the hexagonal phase the bulk modulus decreases while the shear modulus increases. The softening of the bulk modulus in the cubic phase is correlated with the softening of the Fe bonding strength previously observed by nuclear methods, and with a sharp increase in the hydrogen capacity of these compounds. The stiffening of the shear modulus in the hexagonal phase may be correlated with the decrease of the hydrogen capacity in the corresponding compounds.

I. INTRODUCTION

The pseudobinary system $Zr(Al_xFe_{1-x})_2$ possesses interesting hydrogen-absorption properties. The end points $ZrFe_2$ and $ZrAl_2$ absorb very little hydrogen; however, the substitution of small amounts of Al for Fe in $ZrFe_2$ increases the hydrogen capacity sharply.[1] Because Al is a desirable element in any hydrogen-absorbing alloy, it is important to understand thoroughly the influence of Al on the hydrogen absorption. It was suggested[2] that the increased hydrogen absorption is associated with the softening of the lattice. Subsequent Mössbauer[3,4] and nuclear resonant-photon-scattering[5,6] measurements gave evidence for a softening of the Fe bonding strength with increasing x for $0 \le x \le 0.2$. This range of x corresponds with the increased hydrogen absorption. The present experiments were undertaken to investigate any softening associated with long-wavelength acoustic modes and to explore further possible correlations between elastic properties and hydrogen absorption. Ultrasonic measurements were made on a series of compounds and the elastic moduli obtained.

II. EXPERIMENTAL DETAILS

Polycrystalline ingots of the series $Zr(Al_xFe_{1-x})_2$, $0 \le x \le 1$, were prepared in an arc furnace under an argon atmosphere by melting the weighed fractions of the pure metals on a water-cooled copper hearth. X-ray examinations indicated existence of nearly 100% pure Laves phases. Several different batches of $ZrAl_2$ compounds were made, but in all of them weak x-ray $ZrAl_3$ diffraction peaks were found. The $ZrAl_3$ peaks did not show up, however, in a neutron diffractogram.[7] We conclude on the basis of the different penetration depths of x rays and neutrons that $ZrAl_3$ exists only in the surface layer and its total quantity is negligible. This phase is probably caused by a surface segregation of Al possessing a lower surface energy. It may be safely assumed that such minor surface "contaminations" do not influence the ultrasonic measurements. Samples in the approximate shape of rectangular parallelepipeds, 1–2 mm on an edge, were cut from each ingot using a low-speed diamond saw. These saw-cut pieces were then polished into rectangular parallelepipeds for the ultrasonic measurements described below. Resonant ultrasound spectroscopy[8–10] (RUS) was used to measure the elastic constants. With this technique a rectangular-parallelepiped sample was placed corner to corner between two piezoelectric transducers; one transducer was used for the generation and the other for the detection of ultrasonic vibrations. By sweeping the excitation frequency, a large number of the lowest-frequency vibrational eigenmodes of the sample could be measured. Figure 1 shows a segment of the frequency spectrum for a $Zr(Al_{0.30}Fe_{0.70})_2$ parallelepiped. Ten resonances are shown, including two closely spaced lines at approximately 2.10 MHz and another two at 2.20 MHz. The two lines at 2.10 MHz are also shown in the inset. We measured 30–40 resonances for each of the samples. RUS is well suited for the present measurements for at least two reasons: The high accuracy provided by RUS is needed because measurements on different samples are compared, and the volume of a sample required by RUS is less than 1% of the volume required by conventional techniques, which greatly increases the ease of obtaining homogeneous samples.

The elastic constants were determined from the measured frequencies using an iterative method described by Visscher *et al.*[11] and others.[13–16] We fit the measured frequencies using the elastic constant matrix for isotropic

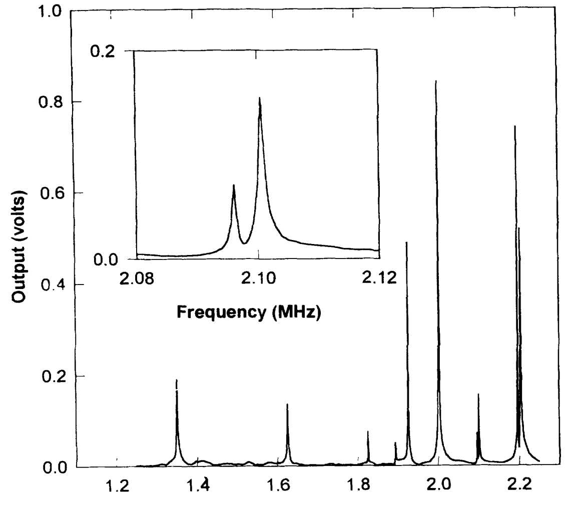

FIG. 1. Resonant ultrasound spectrometer output for a polycrystalline $Zr(Al_{0.30}Fe_{0.70})_2$ parallelepiped of dimensions $0.097 \times 1.04 \times 1.15$ mm^3. Ten resonances are shown, including two closely spaced lines at 2.10 MHz and another two at 2.20 MHz. The inset shows the two lines at 2.10 MHz.

materials. The typical rms deviation between computed and measured results for the lowest 40 frequencies was less than 0.4%. The use of an isotropic elastic constant matrix is only valid if the grain size in these polycrystalline samples is very small compared to the parallelepiped dimensions and if the sample has no voids or cracks. In a few cases we could not obtain satisfactory agreement between measured and computed frequencies. In one such case, an inspection of the sample showed large grains, ~0.1 mm. In other cases, cutting or lapping of the sample revealed cracks or small voids. These problems prevented our obtaining results for the case $x=0$. Results from such samples were not used in the determination of elastic constants. In addition to the measured frequencies, the density of the sample is needed to calculate the elastic constants. We used the density determined from the mass and dimensions of the parallelepipeds. This density agreed excellently with that computed from x-ray data[1,16] for $x > 0.3$. For lower values of x, the macroscopically derived density was about 2% less than the x-ray-derived density.

III. RESULTS AND DISCUSSIONS

Isotropic materials have two independent elastic constants. We fit our measured frequencies to C_{11} and C_{44}. We choose to present the data, however, in terms of the shear modulus G and the bulk modulus B, where

$$G = C_{44} \tag{1}$$

and

$$B = C_{11} - \tfrac{4}{3} C_{44} \; . \tag{2}$$

Results for B and G from measurements on 12 samples are presented in Fig. 2. (The two values for both B and G at $x=0.3$ represent two different samples cut from the same ingot and give an indication of the accuracy of the results. These two samples were quite small, approximately 1 mm on an edge.) The bulk modulus decreases with the substitution of Al for Fe up to $x=0.2$. There is an increase between $x=0.2$ and 0.3. This increase corresponds to the change in crystal structure[1,16] from cubic (C15) to hexagonal (C14) at $x=0.25$. Above $x=0.3$ the bulk modulus continues to decrease with the substitution of Al for Fe. The behavior of the shear modulus is quite different from that of the bulk modulus. The shear modulus hardly changes in the cubic phase; nor does it change at the cubic-to-hexagonal transition. Above $x=0.4$, however, the shear modulus increases with increasing Al content.

The lattice expands approximately linearly with x as Al is substituted for Fe.[1,16] The volume increase on going from $ZrFe_2$ to $ZrAl_2$ is about 20%. The decrease of the bulk modulus with increasing x is probably due in part to the lattice expansion. The bulk modulus appears to decrease monotonically with x, except that the hexagonal phase has a larger bulk modulus than the cubic phase. The behavior of the shear modulus is markedly different from that of the bulk modulus. G changes least for the values of x where B changes most rapidly, and the change in G is opposite to that of B. The increase of G at high x values may be associated with enhanced *p-d* hybridization in the Al-rich phase, leading to a bonding which is stiffer with respect to the angular distortions associated with the shear modulus.

Interesting differences and similarities are found when comparing the present results with those from solution calorimetry,[17] Mössbauer spectroscopy,[3,4] and nuclear resonant photon scattering.[5,6] The solution calorimetry yields the heats of formation of the compounds. The two nuclear techniques measure the Fe bonding strength through the effects of the rms displacement and of the mean kinetic energy of the Fe atoms on the Mössbauer recoilless absorption and resonant-photon-scattering in-

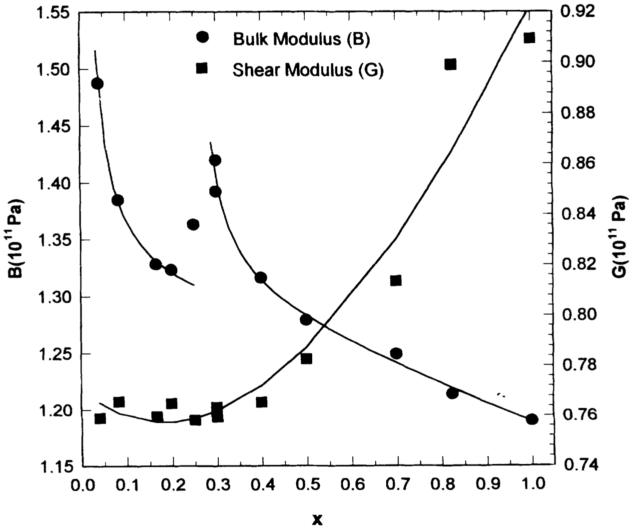

FIG. 2. Bulk and shear moduli for $Zr(Al_xFe_{1-x})_2$ for $0.04 \le x \le 1.0$. The solid lines are simple fits to the data to guide the eye.

tensity, respectively. The bulk modulus, measured by long-wavelength acoustic waves, and both nuclear probes reveal a phonon softening with increasing x in the range $0 \leq x \leq 0.2$. In addition, all four measurements show that the hexagonal phase is stiffer than the cubic phase at the phase boundary. For larger x values, the Mössbauer results show little change, while both the bulk and shear moduli continue to change. The heats of formation vary through the whole x range and exhibit a similar behavior as the Debye temperatures calculated from the present measurements (not shown here).

The decrease of the bulk modulus in the cubic phase as x increases from 0 to 0.2, as well as the softening found by the nuclear probes, is correlated with a strong increase of the hydrogen capacity of $Zr(Al_xFe_{1-x})_2$ over this same x range.[1] The hydrogen capacity of $ZrFe_2$ is essentially zero, while the capacity of $Zr(Al_{0.20}Fe_{0.80})_2$ is almost three H atoms per molecule. In the hexagonal phase the shear modulus increase of 20% is correlated with the hydrogen capacity decrease from the maximum value of about three H atoms per molecule to almost zero. These correlations are in accordance with the "rule of reverse capacity."[2]

IV. CONCLUSIONS

Resonant ultrasound spectroscopy has been used to measure the bulk and shear moduli of the pseudobinary intermetallic compounds $Zr(Al_xFe_{1-x})_2$ for $0.04 \leq x \leq 1.0$. In the cubic (C15) phase, $x < 0.25$, the bulk modulus decreases with increasing x. This decrease is qualitatively similar to the softening of the Fe bonding strength for the same x range as measured by both Mössbauer spectroscopy and nuclear resonant photon scattering. It is significant that the softening measured by all three methods is correlated with a strong increase in the hydrogen capacity of these compounds. The nuclear methods indicate that the Fe bonding strength is stronger in the hexagonal phase at the phase boundary. The ultrasonic results show that the bulk modulus is higher in the hexagonal phase at the phase boundary, but the shear modulus is unaffected by this transition. The relationship of the stiffness to the hydrogen capacity is more complex in the hexagonal phase as compared to the cubic phase. The hydrogen capacity decreases with increasing x in the hexagonal phase. The Mössbauer measurements show little change of the Fe bonding strength in this phase, but the bulk modulus decreases while the shear modulus increases with increasing Al content. The present and previous results on the stiffness in the $Zr(Al_xFe_{1-x})_2$ system indicate that there is a correlation between the distinct hydrogen absorption in this system and *some* of its bonding properties. It is important, in our opinion, to try to understand further these correlations as they may provide useful indications for initiating or halting a hydrogen absorption in certain cases.

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