The specific volumes and viscosities of the Ni-Zr liquid alloys and their correlation with the glass formability of the alloys

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Abstract

The specific volumes and viscosities of the Ni-Zr liquid alloys as a function of temperature are determined by employing a digitizing technique and numerical analysis methods applied to the optical images of the electrostatically levitated liquid alloys. The results show that the specific volume of the $NiZr_2$ alloy is significantly smaller than that of an ideal mixture of the constituting metals, thereby indicating the presence of the associated species in the form of $NiZr_2$. The presence of $NiZr_2$ species can account for the observed properties: the configurational arrest above the melting point under a moderate cooling rate and a relatively small undercooking level prior to crystallization. The results also show that the viscosities of the compound forming alloys are larger than those of the eutectic alloys, thereby indicating the presence of the NiZr and $NiZr_2$ species. The associated species are stable and exist at temperatures well above their melting points. It is concluded that a small specific volume or a large viscosity resulting from the presence of the associated species primarily facilitates the glass formation of the Ni-Zr alloys by slowing down the growth of the crystalline phases.

1. INTRODUCTION

The Ni-Zr alloys are known to be transformed into glasses not only by liquid quenching but also by solid state diffusion.] However, it is not fully understood why the alloys are relatively easy glass formers when they are compared with some other alloys. Glass is a metastable phase which is considered to be a frozen liquid and can be formed if a liquid is undercooked to a temperature where the atomic relaxation time of the liquid exceeds the experimental time scale determined by the cooling rate. In general, a liquid can 'be undercooked to some extent if instantaneous nucleation of a solid at the melting point is avoided. The undercooking level of the liquid depends on many factors including the cooling rate and the local atomic structure of the liquid. The mobility of the liquid atoms determines the relaxation time; therefore, it plays an important role on the glass formability of the liquid. The degree of the mobility depends on the local atomic structure which may be related to the thermophysical properties such as the specific volume and viscosity of the liquid.

The specific volume of a liquid alloy, V_l, generally shows a deviation from that of an ideal liquid mixture of the constituents, Vial. The difference, $\Delta V_E = V_l$ - Vial, is called the excess volume and is usually less than ± 3 % of V_l, where the sign depends on the affinity between the dissimilar atoms.[2] Exceptions are found in some compound forming alloys which show large negative ΔV_E values (up to -30 %). A large negative ΔV_E value is attributed to strong attractive interactions between dissimilar atoms and is indicative of the presence of a chemical short-range order (formation of associated species). The viscosity of a liquid alloy is another measure of the mobility of an individual atom impeded by frictional forces imposed by the surrounding atoms. The viscosity is a function of the liquid temperature and the alloy composition and sometimes shows a maximum value at a compound forming composition, indicating the presence of the associated species. Naturally, the mobility of the associated species is lower than that of a single atom because

of the required coordinated motion of the atoms. It has been suggested that the glass formation is facilitated by the presence of the associated species.[3]

A mixing enthalpy study of the Ni-Zr alloys showed that the associated species existed in the vicinity of Ni_7Zr_2 and NiZr.[4] The study assumed that the species formation was associated with a strong chemical interaction which occurred when the dissimilar atoms were mixed. In the present study, we assume that the species formation can be related to a particular specific volume or viscosity value of the Ni-Zr alloys. For the present measurement, we utilized a unique system which had been developed to measure the thermophysical properties of high temperature materials.[5] The system consists of an electrostatic levitator and non-invasive diagnostic devices. An advantage of the system is the elimination of an instantaneous crystallization catalyzed by the container walls at the melting point. As a consequence, a levitated liquid sample achieves a certain undercooking level prior to the onset of crystallization. Therefore, the present system allows us to measure the specific volumes and viscosities of the liquids not only in the stable state but also in the metastable state (undercooked region).

II. EXPERIMENTAL PROCEDURE

We prepared buttons of the NiZr, $NiZr_2$, $Ni_{36}Zr_{64}$ and $Ni_{24}Zr_{76}$ alloys by induction melting of 99.999% pure Ni and 99.9% pure Zr on a silver boat in an Ar atmosphere. The first two are the compound forming alloys and the last two are the eutectic alloys. A sample of typically 50 mg (-2 mm in diameter) cut from a button was levitated in a high vacuum environment (-10-7 Tom) using the electrostatic force which supported the sample against gravity. The levitated sample was then heated up above the melting point (or the eutectic temperature) by a high intensity xenon arc lamp. Once the sample was melted, it was formed in a nearly spherical shape due to surface tension effects. The temperature of the sample was measured by a pyrometer whose spectral emissivity setting was adjusted at the melting point (or the eutectic temperature) of the alloy.

The sample was held at a high temperature for tens of seconds to establish an initial equilibrium temperature. Then, the high intensity beam was suddenly blocked so that the sample was cooled by radiative heat loss to the surroundings. During this cooling process, the images of the levitated sample were taken using a video camera at the rate of 30 frames per second. After repeating the measurement several times, the sample was retrieved for weight measurement. Next, a metallic sphere whose diameter was precisely known was levitated at room temperature and its images were taken for calibration purposes. The specific volume was determined from the stored images by employing an image digitizing technique and numerical analysis methods. The specific volume as a function of temperature was determined by utilizing the temperature data taken by the pyrometer. The detailed description of the specific volume measurement method has been reported elsewhere.[6,7]

For the viscosity measurement, the liquid sample was held at a constant temperature by adjusting the intensity of the xenon arc lamp. Then, a small sinusoidal electric field whose frequency was close to the resonance frequency of the sample was superimposed to the levitation electrical field for a short time to induce the sample oscillation. The decay of the resonance oscillation after the imposed oscillation was monitored by an optoelectronic device. By analyzing the decay of the oscillation, the resonance frequency of the sample and the decay constant, τ of the oscillation were determined. The resonance frequency can be related to the surface tension, which we will not discuss in this paper. The decay constant can be related to the viscosity, η by the following equation: [8]

$$\eta = \frac{\rho r^2}{5\tau} \qquad (1)$$

where p and r are the density and the radius of the sample, respectively. The measurement was repeated at different holding temperatures to establish the viscosity as a function of

temperature. A detailed description of the viscosity measurement will be reported elsewhere.[9]

III. RESULTS

Figure 1 shows a result of the specific volume measurement in which the specific volume and the sample temperature are shown as a function of time. In this measurement, a liquid $NiZr_2$ sample was cooled from 1650 K. The thermogram (solid line) shows that the liquid is undercooked prior to the onset (indicated by the arrow) of crystallization. The undercooking level is approximately 80 K. Due to recalescence, the sample temperature almost instantaneously rises to the melting point (horizontal portion). Once crystallization is complete, the sample starts cooling again. The specific volume (the solid circles connected by the dotted line) of the liquid gradually decreases as the temperature decreases except a double kink at around 1420 K. The cause of the kink will be discussed later in detail. The data of the liquid/solid mixture and the solid show large scattering due to non-sphericity of the sample. However, it is possible to determine a reasonably accurate specific volume by taking a running average of data because the sample was randomly rotating.

Figure 2 shows the specific volumes of the four alloys as a function of decreasing temperature. The melting point of each alloy is indicated by the arrow. The data of the $Ni_{24}Zr_{76}$ alloy are very close to but slightly smaller than those of the $Ni_{36}Zr_{64}$ alloy. Note that the specific volume of the $NiZr_2$ alloy is significantly smaller than those of the other alloys. Following a practice employed in Ref. 2, the specific volume, V(T) at the temperature, T is fit with the equation,

$$V(T) = V^*\{1 + \alpha(T - T_n)) \qquad (2)$$

where α is the thermal expansion coefficient and T_m is the melting point (or eutectic temperature). The result is summarized in Table 1. The thermal expansion coefficient of $NiZr_2$ is significantly smaller than those of other alloys. Figure 3 shows the specific volumes of the alloys at 1393 K (T_m of the $NiZr_2$ alloy) for close comparison at the same temperature. The solid curve in the figure represents the specific volumes of the ideally mixed liquids. The specific volumes of the ideally mixed liquids are calculated from the data given in Ref. 2. Note that the specific volume of the $NiZr_2$ alloy is significantly smaller than that of the ideal mixture.

The overall error involved in the specific volume measurement is $\pm$ 0.2 % which excludes the additional errors in the temperature and weight measurements. If the emissivity of an alloy gradually changes as the temperature changes, the obtained temperature generally becomes less accurate at temperatures away from the melting point at which the emissivity is adjusted in the present measurement. For the present alloys, the temperature dependence of the emissivities is expected to be small;[4] therefore, the error is conservatively estimated to be $\pm$ 20 K at the farthest temperature from the melting point. Evaporation of a liquid sample during the heating and cooling processes introduces the error in the sample weight which is measured before or after the levitation of the sample. For the present alloys, this error is minimal because of their low vapor pressures.[7]

Table 2 summarizes the results regarding the undercooking level, $\Delta T = T_m - T_N$, the excess volume at the melting point, and the volume change on crystallization; $\Delta V_{ls} = V_l - V_s$, where T_N and V_s are the nucleation temperature and the specific volume of the solid, respectively. As a reference, the data for the constituting metals are also presented.[10] The compound forming alloys, especially $NiZr_2$ shows a smaller undercooking level in comparison to those of other metals and alloys. The ΔV_{ls} values for the NiZr, $Ni_{36}Zr_{64}$ and $Ni_{24}Zr_{76}$ could not be determined because" of severe deformations of the samples due to large shrinkage on crystallization but they should be at least 5 % by considering the

values of the constituting metals. Note that the volume change of the $NiZr_2$ alloy is 1 % which is significantly smaller than those of other alloys and metals.

In order to investigate the double kink observed in the specific volume of the the $NiZr_2$ alloy, an additional measurement was performed. Figure 4 shows the specific volume of the $NiZr_2$ alloy when a sample is cooled from three different temperatures, 1460, 1650 and 1840 K. As is seen, when the sample is cooled from 1840 K (open circles), the deviation from the linear temperature dependence starts around 1500 K. The onset of the deviation shifts to around 1460 K when the sample is cooled from 1650 K (solid circles). However, when the sample is cooled from 1460 K (squares), the deviation does not appear. The melting point, 1393 K is indicated by the vertical line. This result implies that the kink only appears when the sample is rapidly cooled from high temperatures, where "rapidly" is a relative term as opposed to "slowly". The cooling rate of this particular sample by natural radiative heat loss is -32 K/see at the melting point. When the alloy is cooled from 1460 K (this is equivalent to slowly cool the alloy from a high temperature to 1460 K), its specific volume exhibits a linear temperature dependence without the kink. To our best knowledge, the $NiZr_2$ alloy is the first example which exhibits a cooling rate effect above the melting point under a moderate cooling rate. The effect is only temporary; however, and the specific volume eventually returns to the expected value.

The viscosity measurement was performed with a sample taken from the same button when it was possible. Figure 5 shows the viscosities of the alloys as a function of temperature. The melting point of each alloy is indicated by the arrow. Following convention, the viscosity, $\eta(T)$ is fitted with the Arrhenius equation,

$$\eta(T) = \eta_0 \exp(\frac{E}{RT}) \qquad (3)$$

where η_0 is the pre-exponential viscosity, E is the activation energy and R is the gas constant. The results are summarized in Table 3 and also shown in Fig. 5 as the solid curves. The meting points (eutectic temperatures) are indicated by the arrows. Ideally, we should be able to measure the viscosity down to the undercooking limit; however, due to the kinetics of crystallization and the rapid increase in the viscosity, the lowest possible temperature of the measurement is above the undercooking limit. Note that the temperature dependence of the viscosity shows a difference in the compound alloys from that in the eutectic alloys. The overall error is estimated to be $\pm$ 20 %. The main source of the error is due to the difficulties in obtaining consistent decay curves. These difficulties arise from the sample conditions (e.g., degree of surface contamination) and the system conditions (e.g., setting of the levitation control parameters).

IV. DISCUSSION

The specific volume data indicate a strong presence of the associated species in the $NiZr_2$ liquid alloys. In the following, we interpret the observed distinctive properties of the $NiZr_2$ alloy on an assumption of the presence of the $NiZr_2$ species: First, the $NiZr_2$ alloy shows significantly small undercooking compared with those of the other alloys and the metals. This difference should not have arisen from the experimental conditions because the sample preparation and the experimental procedure are the same for all of the alloys. Since the alloy possesses the small ΔV_{ls} value, it is likely that the bonding of the species is similar to that of the compound solid including the lattice parameters. Then, a drastic local structural rearrangement is not required when the liquid is transformed into the solid. According to classical nucleation theory, the nucleation rate, I, is given by the following form

$$I \sim \exp\left(-\frac{\sigma_{sl}^3}{AG^2}\right) \qquad (4)$$

where σ_{sl} and AG are the liquid/solid interracial energy and the free energy difference between the solid and liquid, respectively. Since σ_{sl} is always positive, it acts as a barrier for nucleation. The larger the σ_{sl} value, the more resistant it is to nucleation, which results in a large degree of undercooking prior to the onset of crystallization. As is speculated above, the $NiZr_2$ liquid has a similar local structure to the solid; therefore, misfits should be small when the two phases contact to form the interface. As a result, the interface has a small interracial energy. Thus, the small undercooking of the $NiZr_2$ alloy can be attributed to the small interracial energy.

The kink observed on the specific volume of the $NiZr_2$ alloy can also be caused by the presence of the associated species. If the liquid atoms form the associated species, their mobility is significantly reduced because the movement requires coordinated atomic motions. The large negative ΔV_E value means that the atoms are densely packed in the liquid. In other words, the free volume of the alloy is small, which also contributes to the sluggish atomic movement. It has been suggested that the time-temperature curves generated on cooling such as the thermogram shown in Fig. 1 may be used to study the atomic structure change of the liquid as the temperature changes. [11] Since the heat loss during cooling is purely radiative, the cooling rate of a sample is given as

$$\frac{dT}{dt} = -\frac{\sigma \varepsilon_T A}{mC_p}(T^4 - T_0^4) \qquad (5)$$

where m is the mass, C_p is the specific heat, σ is the Stefan-Boltzmann constant, ε_T is the hemispherical total emissivity, A is the surface area and To is the temperature of the surroundings. By rearranging Eq. (5), C_p/ε_T is given as

$$\frac{C_p}{\varepsilon_T} = -\frac{\sigma A}{m}(T^4 - T_0^4)\frac{dt}{dT} \quad . \tag{6}$$

The dt/dT value can be obtained from the experimental time-temperature curve by taking a derivative. Figure 6 shows C_p/ε_T of the NiZr and $NiZr_2$ alloys as a function temperature. The NiZr alloy shows a gradual increase of C_p/ε_T as temperature decreases. On the other hand, the C_p/ε_T curve of the $NiZr_2$ alloy shows a steep increase in C_p/ε_T which starts around 1460 K, when it exhibits the kink on the specific volume. - However, the steep increase does not appear when the same alloy does not exhibit the kink on the specific volume because it is cooled from a low temperature. Since ε_T is expected to be approximately constant within the temperature ranges of the experiment, the increase in C_p/ε_T is due to the increase in C_p. The main contributions to C_p Of liquids come from the vibrational and configurational entropies. The configurational entropy naturally deceases as the temperature decreases; however, it may also rapidly decrease if all the atomic configurations are not equally sampled due to sluggish atomic mobility. Thus, the steep increase in C_p of the $NiZr_2$ alloy can be attributed to the loss of entropy due to the configurational arrest in the liquid.

The small undercooking level and the configurational arrest are conflicting factors for the glass formability of the $NiZr_2$ liquid alloy. The thermodynamic barrier for nucleation of the solid is relatively small because of the small interracial energy, which means that the solid nuclei can be formed easily. On the other hand, the kinetic barrier for growth is relatively high because of the sluggish atomic mobility, which means that it takes a long time for the nuclei to grow to macroscopic phases. Considering the high glass formability of the Ni-Zr alloys, it seems that the atomic mobility which controls the solid phase growth is the major factor in determining the glass formability of the alloys and the nucleation rate is a minor factor.

The viscosity data indicate the presence of the $NiZr$ and $NiZr_2$ species. As seen in Table 3, the activation energies for viscous flow of the alloys are larger than those given by the experimental correlation, $E/RT_m = 2.4$ which is applicable to most metals, compounds and eutectic alloys. [12] For the compound forming alloys, the large activation energy means the presence of the associated species. For the eutectic alloys, it means the depression of the eutectic temperature below the ideal value. The viscosities of the compound forming alloys are larger that those of the eutectic alloys at high temperatures. This implies that the species are quite stable at temperatures well above the melting points.

The viscosity of the glass forming alloys are known to be better fit by the Vogel-Fulcher-Tammann equation.[12] The equation allows us to estimate the temperature at which the excess configurational entropy or the free volume vanishes. This temperature may be considered to be an ideal glass transition temperature, T_0, because the configurational entropy of the liquid cannot be lower than that of the solid. It is known that the experimental glass transition temperature is typically 50- 100 K above T_0 for most materials. Although the present data, specifically the $Ni_{24}Zr_{76}$ alloy showed the deviation from Eq. (3), we did not attempt to determine T_0 because of the relatively large error involved in the data. We are working on improvements of the viscosity measurement.

V. CONCLUSIONS

The specific volume and viscosity measurements of the Ni-Zr liquid alloys show that the associated species in the form of $NiZr$ and $NiZr_2$ exist in the liquid alloys. The presence of the $NiZr$ species was previously known from the mixing enthalpy study. On the other hand, the $NiZr_2$ species are identified for the first time in the present study. The specific volume data show that the $NiZr_2$ species are densely packed. As a result, the $NiZr_2$ liquid alloy experiences the configurational arrest above the melting point under a moderate cooling rate. The $NiZr_2$ liquid alloy shows the relatively small undercooking level which is attributed to the small interracial energy between the liquid and the solid

because of their similar local structures. On the other hand, the $NiZr$ species are more openly packed according to the specific volume data; however, they are still responsible for the high viscosity. The viscosity data show that the $NiZr$ and $NiZr_2$ species are stable and exist at temperatures well above their melting points. The high glass formability of the Ni-Zr alloys can be attributed to the presence of the associated species which have been known as a facilitator for the glass formation. The presence of the associated species may not be advantageous for suppressing the formation of the solid nuclei but they greatly reduce the solid phase growth rate, which give a chance for the glass to form and grow once the liquid reaches the temperature where the atomic relaxation time exceeds the experimental time scale.

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Table 1. Specific volumes of the liquid alloys represented by Eq. (2)

Alloy	T_m (K)	V_m (cm^3/g)	α (10^{-5} cm^3/g K)
NiZr	1533	0.140	5.58
$Ni_{36}Zr_{64}$	1283	0.145	5.18
$NiZr_2$	1393	0.120	4.39
$Ni_{24}Zr_{76}$	1233	0.144	5.51

Table 2. Summary of AT, AV_E and ΔV_{ls} of the alloys and metals.

Metal or Alloy	Ni	NiZr	$Ni_{36}Zr_{64}$	$NiZr_2$	$Ni_{24}Zr_{76}$	Zr
T_m or T_E (K)	1728	1533	1283	1393	1233	2130
$\Delta T/T_m$ (%)	14	11	17	6	14	15
$\Delta V_E/V_l$ (%)	N/A	5	3	26	7	N/A
$\Delta V_{ls}/V_l$ (%)	6.3			1		11.4

Table 3. Arrhenius constants for the viscosities of the liquid alloys

Alloy	E (kJ/mol)	E/RT_m	η_0 (mPas)
NiZr	63.0	4.9	0.105
$Ni_{36}Zr_{64}$	95.8	9.0	0.0028
$NiZr_2$	67.0	5.8	0.065
$Ni_{24}Zr_{76}$	90.7	8.8	0.0025

Captions

Figure 1. A typical result of the specific volume as a function of time (or temperature) of the $NiZr_2$ alloy. The time-temperature curve (solid line) shows undercooking of the liquid prior to onset of crystallization. The specific volume of the liquid shows a kink at around 1460 K.

Figure 2. The specific volumes of the liquid alloys as a function of decreasing temperature. The melting point (or eutectic temperature) of each alloy is indicated by the arrow.

Figure 3. The comparison of the excess volumes of the alloys at 1393 K.

Figure 4. The specific volume of the $NiZr_2$ alloy when the alloy is cooled from different temperatures, 1840 K (open circles), 1650 K (solid circles) and 1460 K (squares). The kink is apparent.

Figure 5. The viscosities of the liquid alloys as a function of temperature. The data are fitted with the Arrhenius equation which is given by the solid lines. The melting point of each alloy is indicated by the arrow.

Figure 6. The C_p/ε_T values of the $NiZr_2$ and NiZr alloys as a function of temperature. The C_p/ε_T value of the $NiZr_2$ alloy shows a sharp increase when the alloy exhibits the kink on the specific volume.

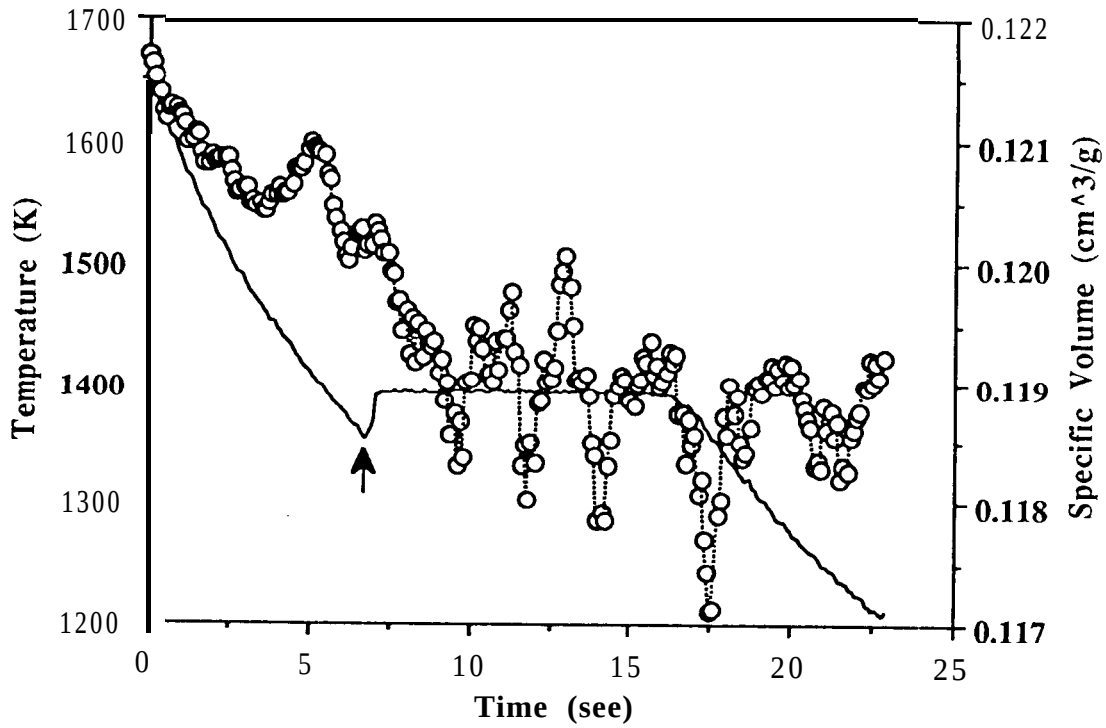
1700
1600
1500
1400
1300
1200
Temperature (K)
0.122
0.121
0.120
0.119
0.118
0.117
Specific Volume (cm^3/g)
0
5
10
15
20
25
Time (see)

Figure 1

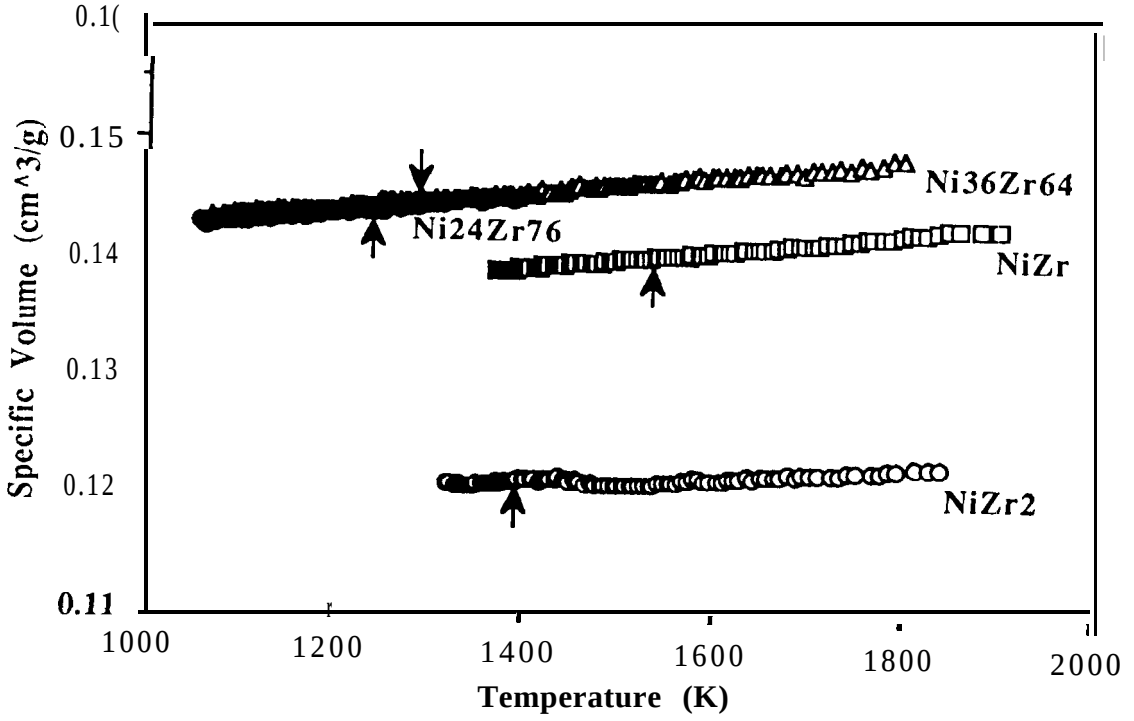
0.1(
0.15
0.14
0.13
0.12
0.11
Specific Volume (cm^3/g)
Ni36Zr64
Ni24Zr76
NiZr
NiZr2
1000
1200
1400
1600
1800
2000
Temperature (K)

Figure 2

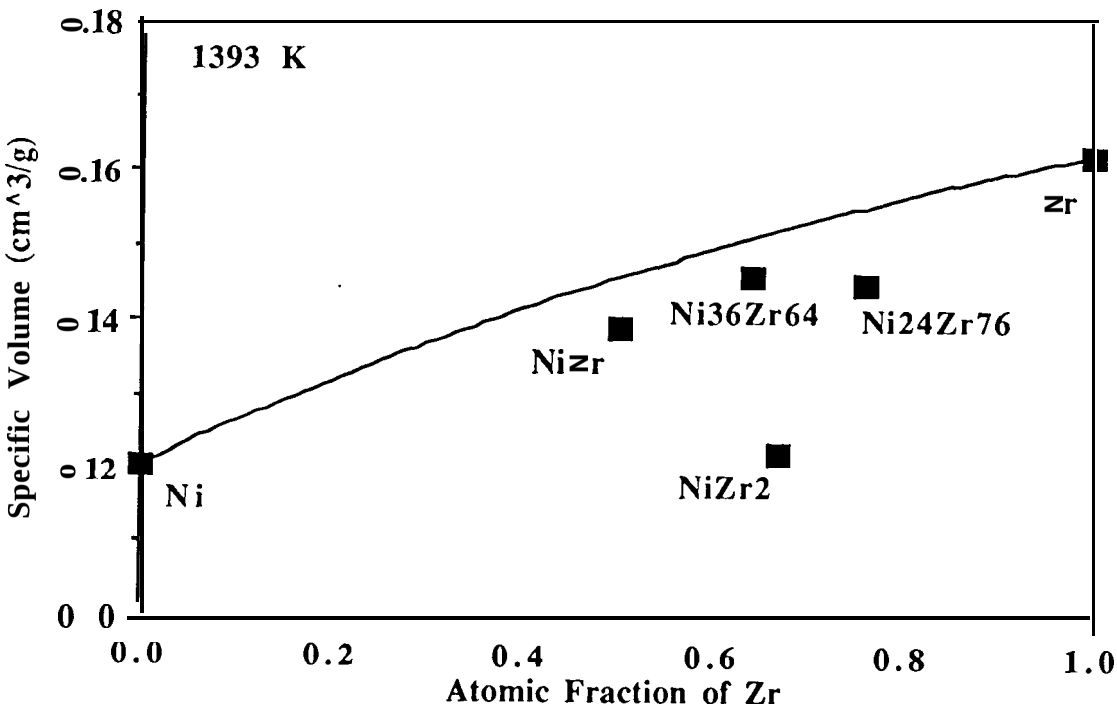
0.18
0.16
0 14
o 12
0 0
1393 K
Specific Volume (cm^3/g)
Ni
Nizr
Ni36Zr64
Ni24Zr76
Zr
NiZr2
0.0
0.2
0.4
0.6
0.8
1.0
Atomic Fraction of Zr

Figure 3

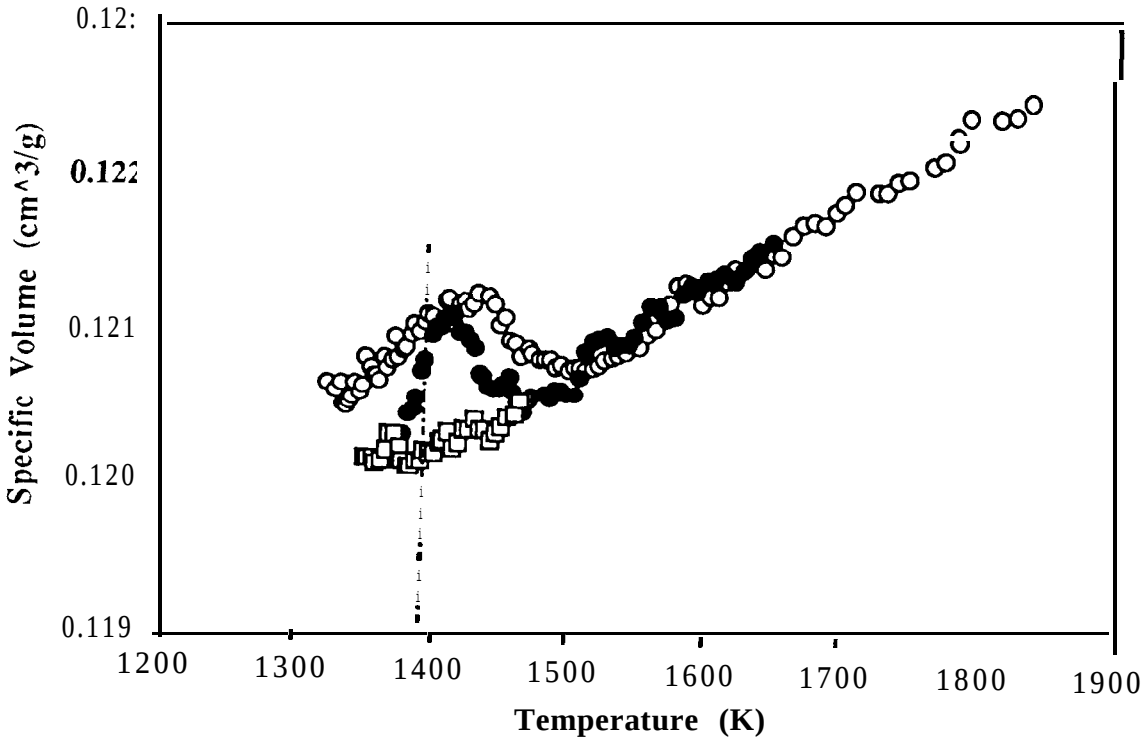
0.12:
0.122
0.121
0.120
0.119
Specific Volume (cm^3/g)
1200
1300
1400
1500
1600
1700
1800
1900
Temperature (K)

Figure 4

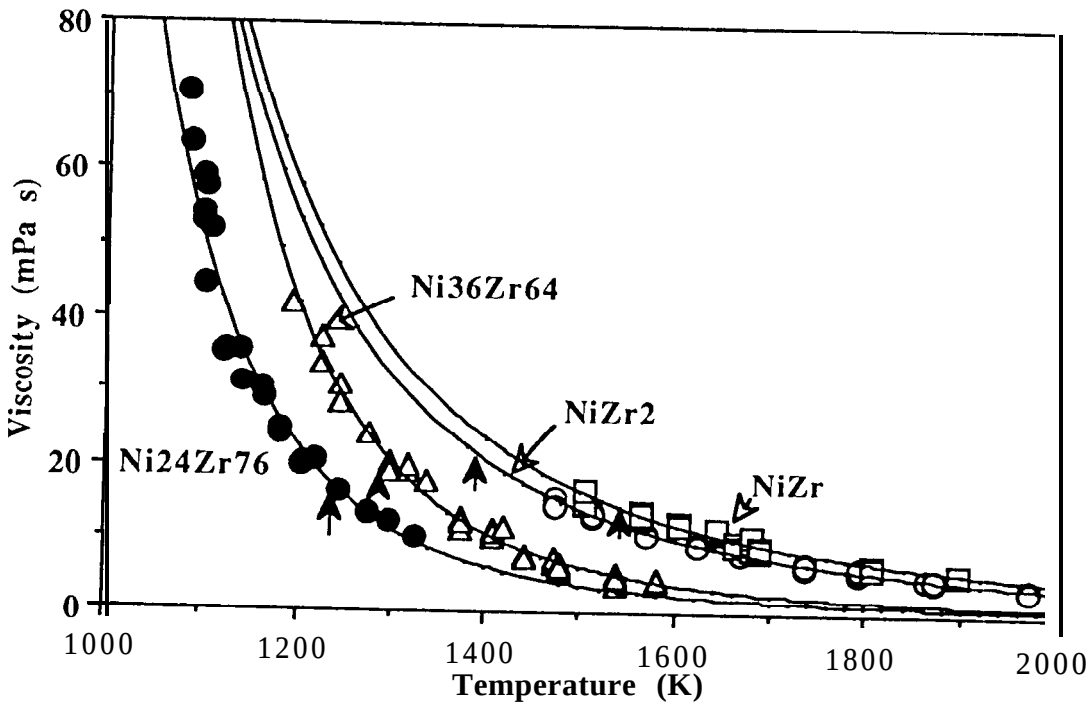
80
60
40
20
0
Viscosity (mPa s)
Ni36Zr64
NiZr2
NiZr
Ni24Zr76
1000
1200
1400
1600
1800
2000
Temperature (K)

Figure 5

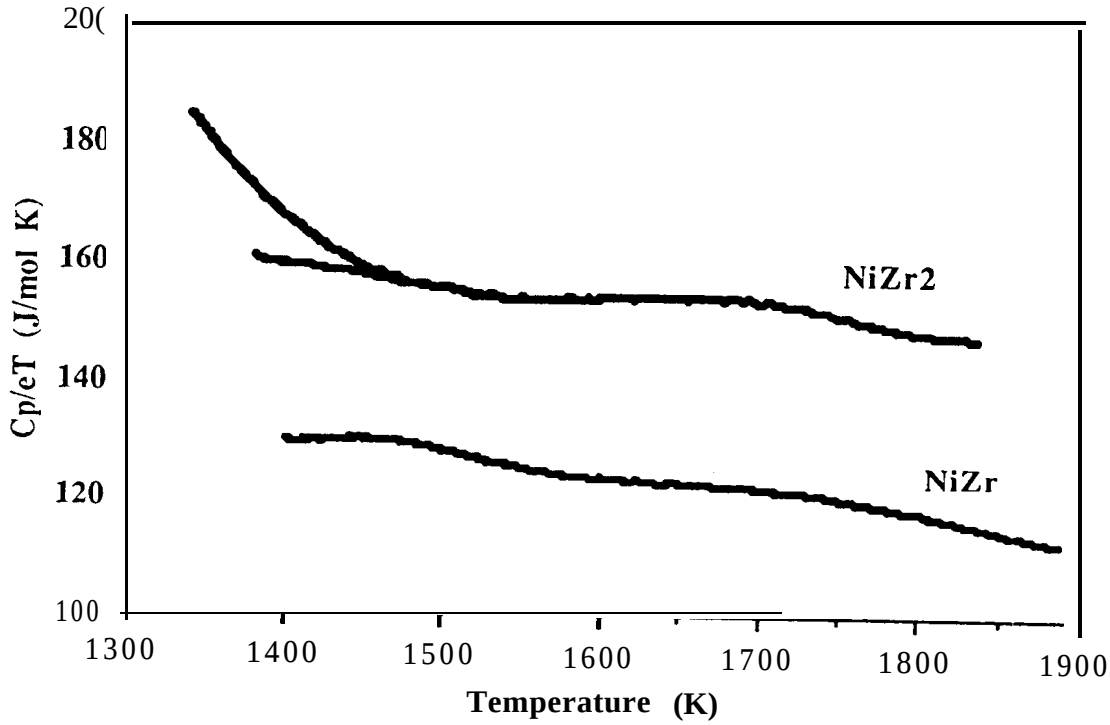
20(
180
160
140
120
100
Cp/eT (J/mol K)
NiZr2
NiZr
1300
1400
1500
1600
1700
1800
1900
Temperature (K)

Fig 6