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# High-temperature thermal expansion of binary alloys of Ni with Cr, Mo and Re: a comparison with molecular dynamics simulations

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**Abstract.** In this paper, thermal expansion studies of the fcc binary alloys $Ni_{1-x}M_x$ (M = Cr, Mo, Re) for $x \leqslant 0.25$ from ambient temperature to 900 K are reported. The results of the changes in the lattice constant $a_0$ and the coefficient of thermal expansion $\alpha$ with $x$ are compared with the recent molecular dynamics (MD) simulations of Mei, Cooper and co-workers providing the first detailed comparison of this type between experiment and theory over an extended temperature and composition range. For NiMo, good agreement is obtained between experiment and theory for the increase in $a_0$ with $x$, the decrease of $\alpha$ with $x$, and the temperature variation of $\alpha$. For NiCr, the agreement is considered to be fair for the increase of $a_0$ with $x$, the decrease of $\alpha$ with $x$, and the $\alpha$ versus temperature data. For the NiRe alloys, the observed decrease of $\alpha$ with $x$ (say near 900 K) is the opposite to the MD simulation prediction of an increase of $\alpha$ with $x$ in this system, although the theoretical predictions at higher temperatures (say 1500 K) tend to be in line with the experimental observations at 900 K. It is argued that effects of magnetic ordering are not responsible for the observed departure from the MD simulation prediction in the NiRe system. A rule-of-mixtures equation gives a linear decrease of $\alpha$ with $x$ for the alloys, in qualitative agreement with the experimental results.

## 1. Introduction

The coefficient of thermal expansion ($\alpha$) of solids is an important thermodynamic quantity which is related to the constant-volume specific heat $c_v$ through the relation

$$\alpha = \gamma c_v / 3B \tag{1}$$

where $B$ is the bulk modulus and $\gamma$ is the Grüneisen parameter (see, e.g., Ashcroft and Mermin 1976). For metals and alloys, $c_v$ includes an electronic contribution proportional to temperature $T$ which is relatively significant only at low temperatures. For $Ni_{1-x}Cr_x$ alloys with $x = 0.09$ to 0.15, and hence a Curie temperature $T_c$ below 20 K, the experimental measurements have verified the proportionality of $\alpha$ to $c_v$ (Simpson and Smith 1982, Kaiser and Smith 1989, Smith *et al* 1991). In equation (1), $B$ and $\gamma$ usually vary only weakly with temperature. For pure Ni with $T_c \simeq 630$ K, Kollie (1977) has reported detailed measurements of $\alpha$ over a wide temperature range including $T_c$.

Nickel-based alloys are well known to have numerous structural applications at high temperatures, due in part to their resistance to oxidation (McNallan *et al* 1991). Consequently there is a great deal of theoretical and experimental interest in the thermal

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and mechanical properties of these alloys. Foiles and Daw (1988) have reported room temperature calculations of $\alpha$ for the fcc metals using an embedded-atom method developed by Daw and Baskes (1984), obtaining good agreement with experimental results. In these calculations, the total energy of the system contains two contributions: the interaction of each atom with the local electron density and a pair interaction reflecting electrostatic interaction between the atoms. Using a similar pair interaction term, Mei *et al* (1993, 1994) have recently developed procedures for modelling the temperature variation of the lattice constant $a_0$ and consequently that of $\alpha$ for the fcc alloys $Ni_{1-x}M_x$ (M = Cr, Mo, Re) for the concentration $x \leqslant 0.16$ using molecular dynamics (MD) simulations. These classical simulations, involving 2048 atoms with periodic boundary conditions to simulate bulk geometry, exclude quantum effects and magnetic ordering. Consequently they are valid only above the Debye temperature $T_D$ and well above the Curie temperature $T_c$. For Ni, $T_c \simeq 630$ K and $T_D \simeq 450$ K. Upon alloying with Cr, Mo and Re, $T_c$ falls dramatically towards zero, as discussed later, whereas $T_D$ for the alloys is not known. However, it is not expected to vary significantly since $T_D = 630$ K, 450 K and 430 K respectively for Cr, Mo and Re. It is therefore clear that to check the predictions of MD simulations, experimental measurements of $\alpha$ for suitable alloys need to be carried out at high temperatures.

In this paper, we report measurements of the temperature variation (300 to 900 K) of $\alpha$ for Ni and for eight alloys of $Ni_{1-x}M_x$ (M = Cr, Mo, Re) for $x \leqslant 0.25$ and compare the results with the MD simulation of Mei *et al* (1993, 1994). As far as we are aware, this work presents the first detailed comparison between the values of $\alpha$ obtained from MD simulations and those from experiments over an extended temperature and composition range for an alloy system. This comparison shows that for NiMo and NiCr, the predictions of the MD simulations in terms of the variations of $\alpha$ with $x$ and $T$ are in good agreement with the experimental observations, whereas for the NiRe system, the experimentally observed decrease of $\alpha$ with $x$ is opposite to the prediction of an increase of $\alpha$ with $x$. In the following sections, the details of the experimental procedures, experimental results and a discussion of them, along with a comparison with the results of the MD simulations, are given. The possible effects on $\alpha$ of magnetic ordering are also discussed.

## 2. Experimental procedures

Samples of nickel-based alloys were prepared by arc melting appropriate amounts of high-purity metals (Johnson–Matthey) in a purified argon atmosphere. The button-form samples were remelted five times to ensure uniformity. These samples were then wrapped in tantalum foil and homogenized in argon atmosphere at 1000 °C for 120 hours; this was followed by furnace cooling. These silvery buttons were then cut into rectangular parallelepipeds ($4 \times 4 \times 10$ mm) for thermal expansion measurements. The elemental analysis of NiCr samples by Galbraith Laboratories (Knoxville, TN) yielded values within $\pm 1\%$ of the nominal compositions. Consequently, for all of the samples, the quoted percentages are the nominal compositions.

All of the samples were x-ray analysed for the fcc phase expected for these alloys using a Rigaku D/Max diffractometer with Cu K$\alpha$ radiation. As shown in figure 1 for selected alloys, only lines expected for the fcc structure are observed, except for for the heavily doped Ni–25%Re alloys which also contain an admixture of the hexagonal phase of pure Re. The fcc Bragg lines are used to determine the lattice constant $a_0$. For some samples, the temperature dependence of $a_0$ was also measured with the x-ray diffractometer.

The bulk of the data on thermal expansion reported here were obtained with a home-designed, computer-controlled, fused-quartz push-rod dilatometer, somewhat similar in
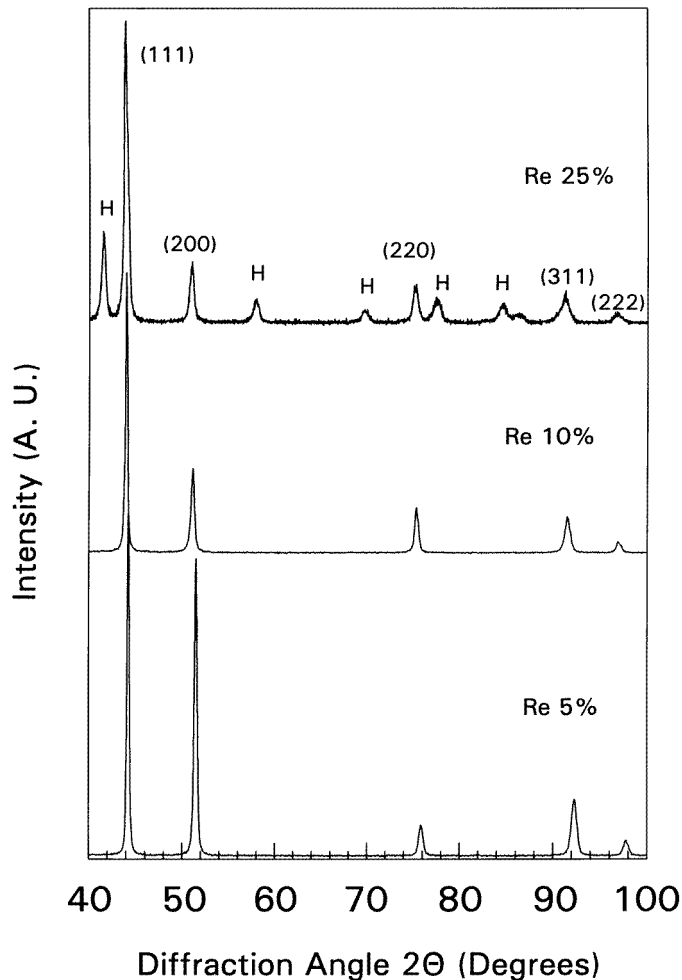
**Figure 1.** X-ray diffractograms of representative binary alloys. Miller indices of the fcc phase are shown. Lines marked 'H' represent the hcp phase of Re in the two-phase $Ni_{75}Re_{25}$ alloy.

design to that used by Kollie for measurements on Ni. The apparent thermal expansion $d\ell$ was measured with a linear variable differential transformer (Lucas–Schaevitz) while the temperature was measured with a calibrated chromel–alumel thermocouple with an ice point reference. A Macintosh SE computer recorded the temperature and $d\ell/\ell$ ($\ell$ refers to the room temperature length). The plots of $d\ell/\ell$ versus temperature were fitted to third-order polynomials whose derivative yielded

$$\alpha = \frac{1}{\ell}\left(\frac{d\ell}{dT}\right). \tag{2}$$

Although this procedure smoothes out the local fluctuations in the calculated $\alpha$, it does yield accurate values for the changes in $\alpha$ with $x$ and temperature. On the basis of five independent measurements, the uncertainty in $\alpha$ is estimated to be $\pm 4\%$. The whole system and procedure was checked by making measurements on pure copper. Magnitudes of $\alpha$ are expressed in units of $10^{-6}$ K$^{-1}$ throughout the paper. For comparison, we note that the

magnitudes of the room temperature $\alpha$ for Ni, Cr, Re and Mo are 13.4, 6.0, 6.2 and 5.0 respectively (Touloukian *et al* 1975).
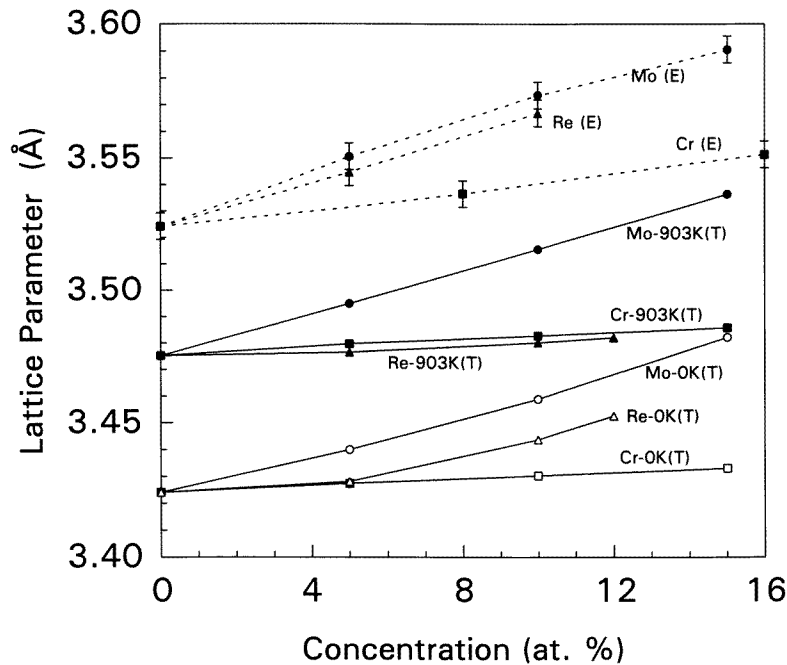


**Figure 2.** The variation of the lattice parameter $a_0$ with atomic percentages of Cr, Mo and Re in the $Ni_{1-x}M_x$ alloys. E represents experimental results obtained from x-ray diffraction and T represents theoretical predictions of Mei *et al* (1994) with the lower set from quantum mechanical calculations at 0 K and the middle set from MD simulations at 903 K.

## 3. Results and discussion

The lattice parameter $a_0$ for the single-phase fcc alloys is plotted in figure 2 against $x$, the concentration in at.% of Cr, Mo and Re, where E represents experimental results at room temperature and T the theoretical predictions (Mei *et al* 1994). Two sets of theoretical curves are shown: the lower set for 0 K obtained using full-potential, quantum mechanical, total energy calculations including magnetic ordering effects and the middle set for 903 K obtained from the classical MD simulations, since these simulations are strictly valid only well above $T_D$ and $T_c$ as noted earlier. (These theoretical predictions are from Mei *et al* (1994), although these plots do not appear there.) For the experimental results, room temperature data are plotted for comparison. In figure 3, XRD data for $a_0$ versus temperature for some of the alloys show that total changes in $a_0$ over the temperature range of the measurements is <1% so changes in $a_0$ with alloying are more significant than those with temperature. Therefore, the comparison shown in figure 2 at different temperatures is meaningful.

The expansion of the lattice upon alloying is evident from both theory and experiment (figure 2). Quantitatively, the best agreement between experiment and theory, as regards the relative change of $a_0$ with $x$, is observed for the NiMo alloys, whereas for the NiCr
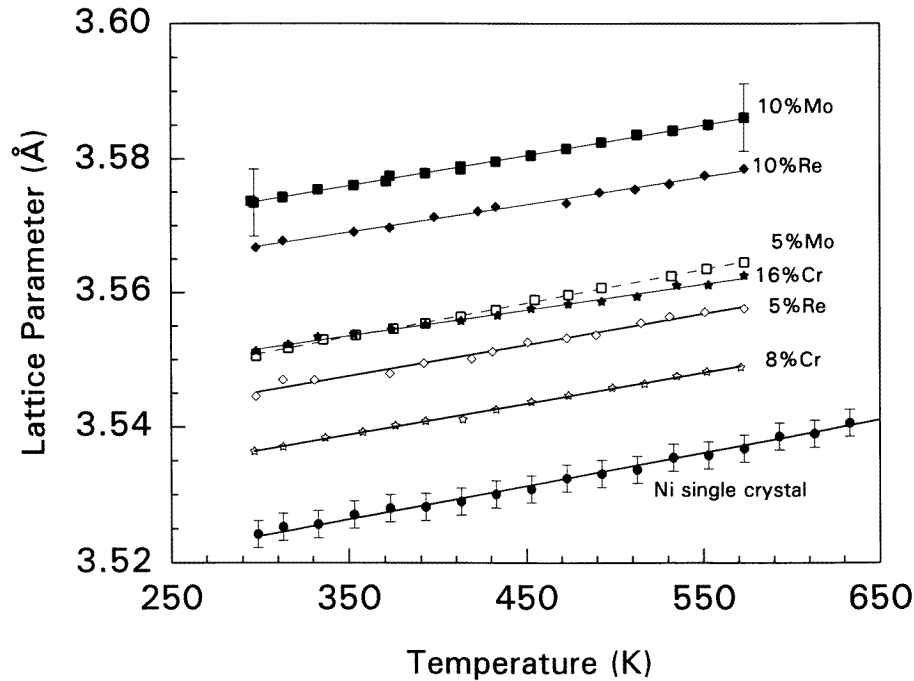
**Figure 3.** Temperature variations of the lattice parameter $a_0$ as determined from x-ray diffraction for the $Ni_{1-x}M_x$ alloys. Representative error bars at a few selected temperatures are shown.

and NiRe alloys, the calculated increases in $a_0$ are lower than the experimental increases. The 0 K, quantum mechanical, total energy calculations provide changes in $a_0$ with $x$ in excellent agreement with the experiment. In absolute terms, the theoretical $a_0$-values are within about 2% of the experimental values once allowance is made for the temperature dependence of $a_0$. This is considered to be an excellent agreement considering that there are no fitting parameters in the calculations. Since $\alpha$ is calculated from $a_0(T)$ in both theory and experiments, this comparison of $a_0$ provides a good test for the theory. The experimental changes in $a_0$ with $x$ give the following ionic radii, assuming close-packed fcc structure: Ni: 1.246 Å; Cr: 1.291 Å; Re: 1.383 Å; Mo: 1.404 Å. These magnitudes are in good agreement with those quoted in the literature (Ni: 1.25 Å; Cr: 1.28 Å; Re: 1.38 Å; Mo: 1.40 Å) (Kittel 1986). Alternatively, the same data can be used to determine $V$, the effective volume per atom, using the equation $a_0^3 = 4V$ and extrapolating the data on $a_0(x)$ versus $x$ to $x = 1$. This analysis yields $V = 10.935, 12.121, 14.572$ and $15.105$ Å$^3$ for Ni, Cr, Re and Mo respectively.

In principle, it is also possible to determine $\alpha$-values from the plots of $a_0(T)$ versus $T$ of figure 3 determined from XRD measurements. However, in these measurements, we are not able to resolve $a_0$-values less than 20 K apart. Consequently, the accuracy in the calculations of the temperature variation of $\alpha$ from these data is quite limited. For the alloys, the average values of $\alpha$ as determined by XRD in the temperature range of 25–300 °C are as follows: Ni: 13.9; $Ni_{92}Cr_8$: 13.0; $Ni_{84}Cr_{16}$: 10.9; $Ni_{95}Mo_5$: 14.1; $Ni_{90}Mo_{10}$: 12.6; $Ni_{95}Re_5$: 13.1 and $Ni_{90}Re_{10}$: 11.6. These magnitudes are in general agreement with those determined from dilatometry, as seen below.
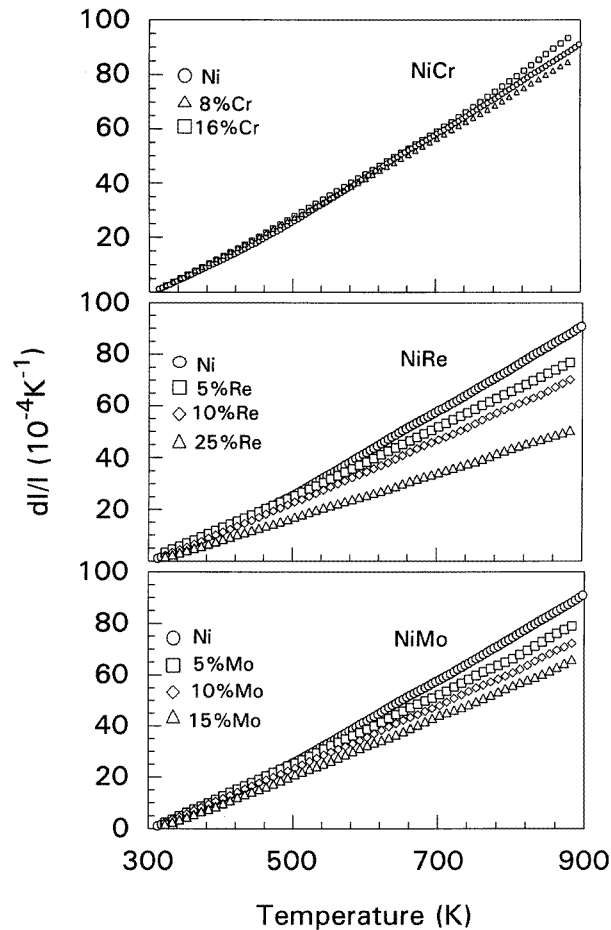
**Figure 4.** The fractional thermal expansion $d\ell/\ell$ versus temperature for Ni, NiCr, NiRe and NiMo alloys as determined from dilatometry.

The plots of the thermal expansion $d\ell/\ell$ versus temperature measured by dilatometry are shown in figure 4 for the NiCr, NiRe and NiMo alloys. It is clear that addition of Cr has the least effect on thermal expansion whereas alloying with Re and Mo significantly lowers $d\ell/\ell$, particularly at higher temperatures. This may not be surprising since addition of Cr has the least effect on the lattice constant (figure 2), because the atomic volumes of Ni and Cr are comparable.

The temperature variations of the $\alpha$-values calculated from the $d\ell/\ell$ versus temperature plots using the procedures outlined earlier are shown in figure 5. Again, the addition of Cr has the least effect on $\alpha$ whereas the addition of Re has the most. Note that the $Ni_{90}Re_{10}$ alloy has an essentially temperature-independent $\alpha$ whereas the two-phase $Ni_{75}Re_{25}$ has the lowest $\alpha$ of all the alloys investigated here. Since the room temperature $\alpha$-values for Cr, Mo and Re are essentially equal (Touloukian *et al* 1975) as noted earlier, the different results observed here for NiCr, NiMo and NiRe alloys show that $\alpha$-values for alloys are not simply averages of those of their elements. Some discussion on this point is given later.

The theoretical results of the MD simulations on the temperature variations of $\alpha$ for
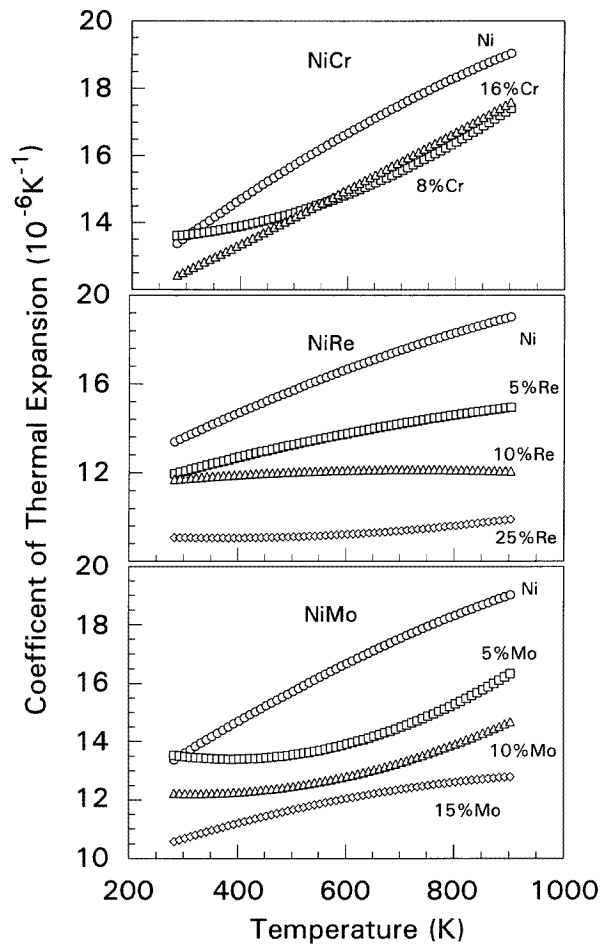
**Figure 5.** The coefficient of thermal expansion versus temperature for Ni, NiCr, NiRe and NiMo alloys as determined from polynomial fitting of the data in figure 4.

the NiCr, NiMo and NiRe alloys (reproduced from Mei *et al* 1994) are shown in figure 6. As noted earlier, the accuracy of these classical simulations is most reliable well above the Debye and Curie temperatures (450 and 630 K respectively for Ni). Consequently, we plot in figure 7 the variation of the $\alpha$s with $x$ (at.% of Cr, Mo and Re) at 903 K, the highest temperature of our measurements, and compare these results with the theoretical predictions of Mei *et al* for 903 K. Examining these comparisons in figures 5–7, the following points are noted.

(i) The best quantitative agreement between theory and experiment, in terms of variations with both $x$ and $T$, is observed for the NiMo system. The prediction of the theory of a nearly temperature-independent $\alpha$ for the 15% Mo alloy at high temperatures and a strongly temperature-dependent $\alpha$ for the 10% Mo alloy are clearly borne out by the experiments. It is noted that the NiMo system also yields the best quantitative agreement in the $a_0$ versus $x$ data (figure 2).

(ii) For the NiCr alloys, the agreement is considered fair, in that similar trends of the
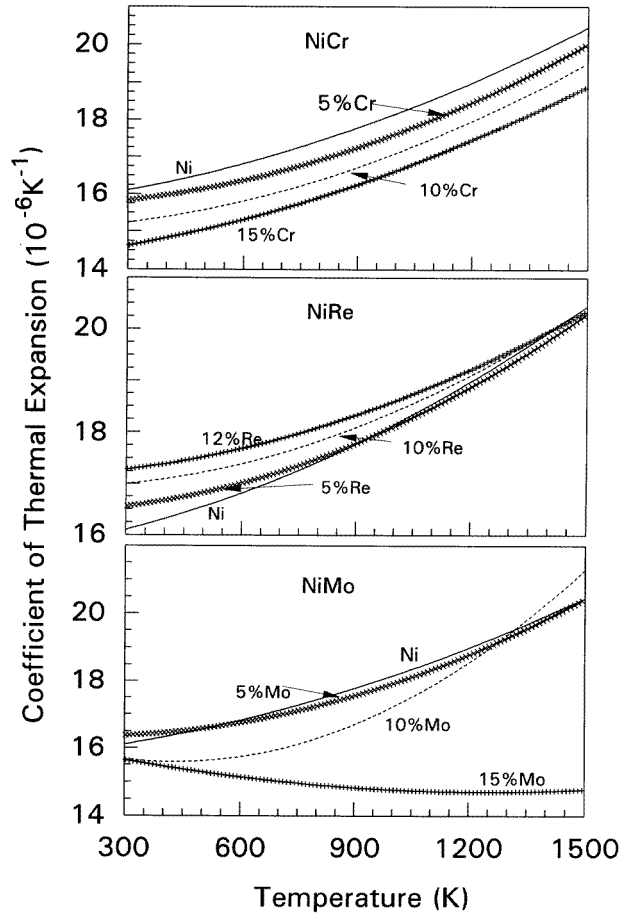
**Figure 6.** The coefficient of thermal expansion versus temperature for Ni, NiCr, NiRe and NiMo alloys as calculated in molecular dynamics simulations by Mei *et al* (1994).

variations of the $\alpha$s with $x$ and $T$ are observed in the simulations and in the experiments.

(iii) For the NiRe alloys, the experimental results do not match the theoretical predictions of the increase of $\alpha$ with $x$ at the lower temperatures. Experimentally, the largest decrease of $\alpha$ with $x$ observed here is for the NiRe system and it is for this system that the MD simulations show the largest divergence from the experiment. At present, we have no explanation for this disagreement, although we note that at high enough temperatures in the simulations (figure 6), there is a reversal in the trend of the change of $\alpha$ with $x$ even for the NiRe alloys, in line with the experimental results.

We next compare our results with the available measurements reported in the literature. For Ni, the best available measurements are probably those of Kollie (1977), yielding values from $\alpha = 12.89$ at 300 K to $\alpha = 16.64$ at 763 K. Our measurements give essentially similar magnitudes and temperature variations. The sharp peak in $\alpha$ observed near the Curie temperature $T_c \simeq 630$ K in Kollie's data has been smoothed out in our data by the polynomial fitting over an extended temperature range. However, a point of inflexion is clearly evident near $T_c$ in the plots of $d\ell/\ell$ in figure 4 for Ni, so a peak at $T_c$ in the $\alpha$-variation for Ni is
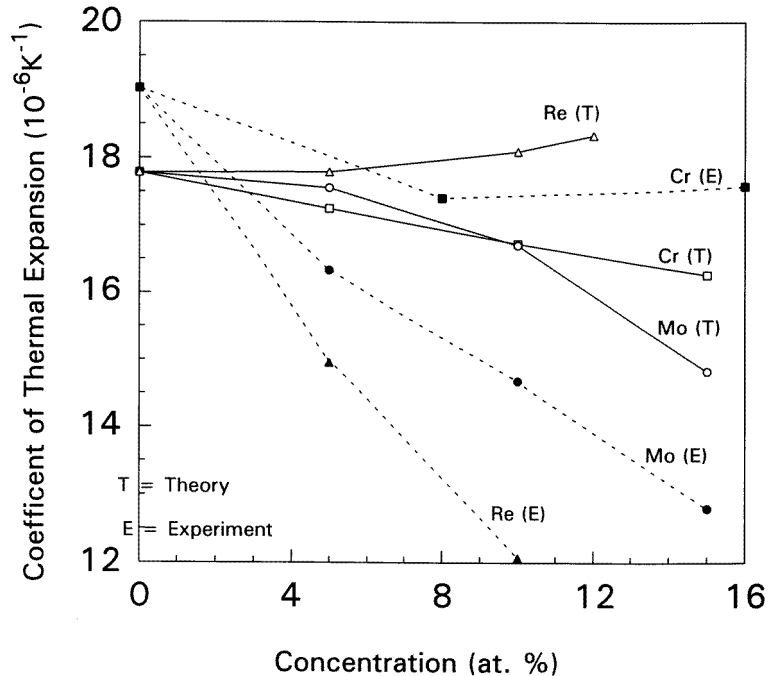
**Figure 7.** Variations of the coefficients of thermal expansion at 903 K against the concentration of Cr, Mo and Re in the binary alloys where T (E) represents theoretical (experimental) results.

present if a sliding polynomial fitting procedure involving just a few data points at a time is used. Since the MD simulations ignore the magnetic effects anyway, the polynomial fitting used here for comparison with theory is more appropriate. From the measurements made by Suh *et al* (1988) on the thermal expansion of nickel and molybdenum, the following $\alpha$s determined by dilatometry are foun Ni: 13.0 at 293 K to 17.7 at 900 K; Mo: 5.1 at 293 K to 6.8 at 900 K.

The effects of ferromagnetic ordering on the $\alpha$s for the Ni-based alloys are considered next. For $Ni_{1-x}Cr_x$ alloys, $T_c$ and magnetic moment decrease dramatically with $x$, both approaching zero for $x \simeq 0.12$ (Smith *et al* 1991, Gregory and Moody 1975). On the basis of these studies, we estimate $T_c \simeq 400$ K (100 K) for $x \simeq 0.05$ (0.1), so the high-temperature comparisons made here for the alloys are well above $T_c$. Simpson and Smith (1982) have measured $\alpha$ for $Ni_{1-x}Cr_x$ for $x = 9$, 9.8, 11, 12, 13, 14 and 15% so as to bracket the paramagnetic-to-ferromagnetic transition for $x_c \simeq 12\%$. These measurements carried out below 20 K (since $T_c$ for these materials is low) show that for $x > x_c$, the paramagnetic alloys have values of $\alpha$ higher than that for ferromagnetic alloys for $x < x_c$. These authors conclude that as $x$ is reduced through $x_c$ as the ordering goes from paramagnetic to ferromagnetic, there is a net *decrease* in $\alpha$ which can only be associated with ferromagnetism. Thus it appears that ferromagnetism affects $\alpha$ in two ways: first, there is a $\lambda$-type anomaly around $T_c$ which can be separated from the smoothly varying temperature dependence of $\alpha$, as, e.g., was done by Kollie (1977) for Ni, and, secondly, there is a negative weakly temperature-dependent contribution due to magnetostriction which is more difficult to separate (Smith *et al* 1991). Comparing the $\alpha$-data for Ni ($T_c \simeq 630$ K) with the MD simulations, we note that at 903 K, the experimental value is about 5% higher than the

theoretical value, whereas at room temperature, the experimental value is about 20% lower than the theoretical result. Considering that the MD simulations do not include magnetic effects, the above results are easily understood if a negative, weakly temperature-dependent, contribution to $\alpha$ from ferromagnetic ordering is assumed. There may be some relationship between the measured $\alpha$ and the saturation magnetic moment of the alloys, as in invars (Chikazumi *et al* 1968).

The discrepancy for the NiRe system between the experimental results and the MD simulations in terms of the change of $a_0$ and $\alpha$ with $x$ need additional attention. Our initial measurements (Babu *et al* 1996) of the magnetic properties of the alloy samples used here show that the drop in $T_c$ with $x$ for Mo and Re is similar to that observed for the NiCr system, so at the temperatures of the comparison (903 K), the magnetic effects should be entirely negligible. Consequently we do not believe that the neglect of the magnetic effects in the MD simulations can be the source of the discrepancy observed for the NiRe system. The microstructure of the NiRe alloys exhibits a dendritic nature, in considerable contrast to the microstructure observed for the NiCr and NiMo system. However, we are not aware of any studies relating the microstructure to the calculation of $\alpha$, although it is noted that all of the grains here have a single-phase fcc lattice. Consequently, that is not likely to be the cause of the discrepancy either.

In their paper, Mei *et al* (1994) have commented on the different predictions for the NiRe system. Their argument is as follows: the total energy of the system consists of two terms, a volume-dependent term which should give an increase in $\alpha$ if the lattice expands on alloying and a pair potential term which may favour or militate against the above expansion. Since interactions between different species are different, Mei *et al* argue that the Ni–Re interaction leads to an enhanced value of the Grüneisen parameter $\gamma$ in equation (1) thereby increasing $\alpha$. The experimental results presented here suggest that this argument may need to be re-examined.

Using a simple rule-of-mixtures equation

$$\alpha = \sum_i \alpha_i V_i \tag{3}$$

(where $V_i$ denotes the volume fraction of each atom in the alloys), atomic volumes determined earlier from the data of figure 2, and the room temperature value $\alpha = 13.4, 6.0, 6.2$ and $5.0$ for Ni, Cr, Re and Mo respectively, one can determine the variation of $\alpha$ with $x$ for the alloys. This calculation gives a linear decrease of $\alpha$ with $x$ for all three cases with the slopes $d\alpha/dx = -8.1, -9.1$ and $-10.9$ (in units of $10^{-6}$ K$^{-1}$) for Cr, Re and Mo respectively between $x = 0$ and $x = 0.16$. In actual numbers, these slopes correspond to changes in $\alpha$ from 13.4 for $x = 0$ to 12.10, 11.95 and 11.66 for Cr, Re and Mo respectively for $x = 0.16$. The experimental percentage drops observed in figure 7 at 903 K between $x = 0$ and $x = 0.16$ are about 8% for Cr, 32% for Mo and >40% for Re. Thus the experimental decrease in $\alpha$ with $x$ for Mo and Re is three to four times larger than the prediction of the simple rule-of-mixtures equation whereas for Cr the experimental and predicted values are quite comparable. It should be noted that the predicted decrease in $\alpha$ is the result of the lower values of $\alpha$ for Cr, Re and Mo relative to that of Ni whereas the larger size of Cr, Re and Mo relative to Ni has the effect of increasing $\alpha$ as argued by Mei *et al* also. Thus the simple rule of mixtures seems to work best when the atomic volumes of the atoms in the alloy are not too different.

In summary, the experimental results and their comparison with the MD simulations for $\alpha$ presented here show good agreement for the NiCr and NiMo systems, whereas for the NiRe system, the observed disagreement warrants further attention.

## Acknowledgments

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