Effects of Re concentration on the expansivity of NiRe alloys to 1200 K

V Suresh Babu and Mohindar S Seehra†

Physics Department, West Virginia University, Morgantown, WV 26506-6315, USA

Abstract. Measurements of the thermal expansion $d\ell/\ell$ and hence the coefficient of thermal expansion α are reported for $Ni_{100-x}Re_x$ alloys ($x = 0$, 5, 8, 10, 12, 16 and 25%) in the temperature range of 300 to 1300 K using a dilatometer. Room temperature x-ray diffraction studies show that for $x \geqslant 12\%$, a small fraction of Re begins to precipitate out, in addition to the dominant face-centred cubic (fcc) phase whose lattice constant increases linearly with x. The variations of α with x plotted at selected temperatures of 503, 903 and 1203 K shows that for $x \leqslant 10\%$, α decreases with increasing x at 503 and 903 K, whereas it remains practically constant with x at 1203 K. The latter result is in agreement with the predictions of Mei *et al* (1994 *Alloy Modeling and Design* ed G M Stocks and P E A Turchi (Warrendale, PA: TMS Publishing)) using molecular dynamics simulations. The variation of α with x shows a minimum at $x = 12\%$ at all temperatures. The possible role of shear stresses in the dendritic grain structure of these alloys on measured α below 1000 K is discussed.

1. Introduction

There has been a great deal of experimental and theoretical interest in the structural, thermal and mechanical properties of nickel-based alloys, partly because of their numerous structural applications at high temperatures (Bradley 1988, McNallan *et al* 1991). The coefficient of thermal expansion (often referred to as CTE or α) of a material is an important thermodynamic quantity (see e.g. Mukherjee *et al* 1996) which is also related to the constant-volume specific heat c_v through the relation $\alpha = \gamma c_v/3B$ where γ is the Grüneisen parameter and B is the bulk modulus. In a recent paper, Mei *et al* (1994) have modelled the temperature variation of α for the faced-centred cubic (fcc) alloys $Ni_{1-x}M_x$ ($M =$ Cr, Mo, Re) using molecular dynamics simulations, excluding quantum effects and magnetic ordering. Consequently, these simulations are valid only above the Curie temperature T_c (≈ 630 K for Ni) and the Debye temperature T_D (≈ 450 K). Experimental verifications of the results of these simulations, therefore, require measurements of α at elevated temperatures. Measurements of α for NiCr, NiMo and NiRe fcc alloys for temperatures up to 900 K have been reported recently by us (Pavlovic *et al* 1996) and compared with the results of the simulations of Mei *et al* (1994). For NiCr and NiMo fcc alloys, excellent agreement with the results of the simulations was reported both in the variation of α with concentration (x) and temperature. For NiRe alloys, the simulations predict an increase of α with increasing x near room temperature whereas in the temperature range of 1200 to 1500 K there is no significant change of α with x. Since our earlier measurements were limited to temperatures

† E-mail address: mseehra@wvu.edu.

below 900 K, the above high-temperature prediction was not verified. In this work, we have extended the measurements of α for NiRe alloys to about 1200 K, allowing comparison with the predictions of the molecular dynamics simulations. We also report that the $Ni_{88}Re_{12}$ alloy has the lowest α at all temperatures, although the alloys for $x \geqslant 12\%$ are not single phase fcc systems but contain hexagonal close-packed (hcp) Re as the second phase. Details of these results are presented below.

2. Procedures, results and discussion

The experimental procedures and the samples used here are the same as reported in our recent work (Pavlovic *et al* 1996), except that the temperature capabilities of the dilatometer were extended to 1300 K. The values of α reported here are computed from the measured fractional dilation $d\ell/\ell$ (measured by a push-rod dilatometer, Pavlovic *et al* 1996) by computer-fitting several consecutive data points to a polynomial, determining the slope at the median point and then sliding the polynomial. Using this procedure, the computed values of α near the end points (300 and 1300 K) are not expected to be reliable and consequently they are not included in our discussion and plots.

In figure 1, we show the x-ray diffractogram of $Ni_{100-x}Re_x$ alloys for $x = 10$, 12 and 16%. Lines marked 'H' are due to the hcp phase of Re and they first become noticeable for $x = 12\%$. Thus for $x = 12\%$, we have a two-phase system, the fcc phase of the alloy and the hcp Re. This is in agreement with the known phase diagram of the Ni–Re system, showing the room temperature solubility of Re in Ni is limited to about 12 at.% (Okamoto
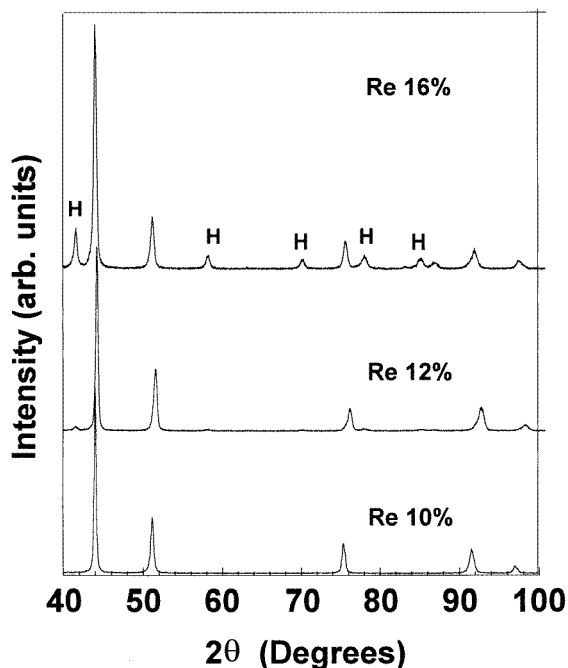

Figure 1. Room temperature x-ray diffractograms of $Ni_{100-x}Re_x$ for $x = 10$, 12 and 16%. H marks the line positions for the hcp Re phase which become clearly evident for $x = 16\%$. Lines for $x = 10\%$ are due to the fcc phase.

1991, Nash and Nash 1985). The variation of the lattice constant of the fcc phase with x (figure 2) also shows a drop in the linear variation of the lattice constant for $x = 12\%$. This confirms that for $x \geqslant 12\%$, only a part of the Re goes into the fcc phase, the remaining precipitating out as hcp Re as seen in the x-ray diffractograms (figure 1). As a comparison, for NiCr and NiMo systems, single phase fcc alloys were obtained for x up to at least 16% (Pavlovic *et al* 1996).
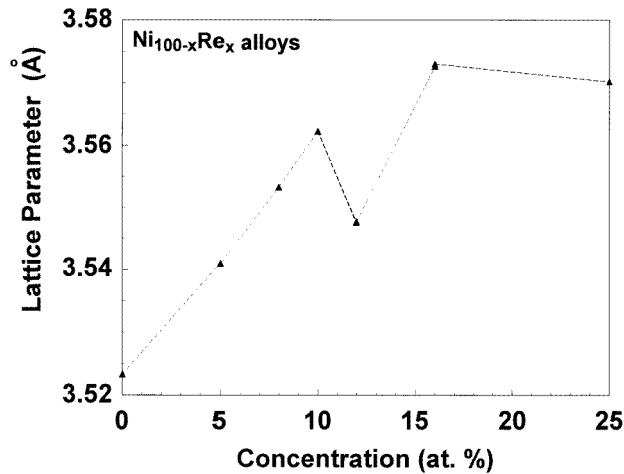

Figure 2. Variation of the room temperature lattice constant of the fcc phase with x for $Ni_{100-x}Re_x$ alloys. The departure from linearity at $x \geqslant 12\%$ is due to the precipitation of some Re.
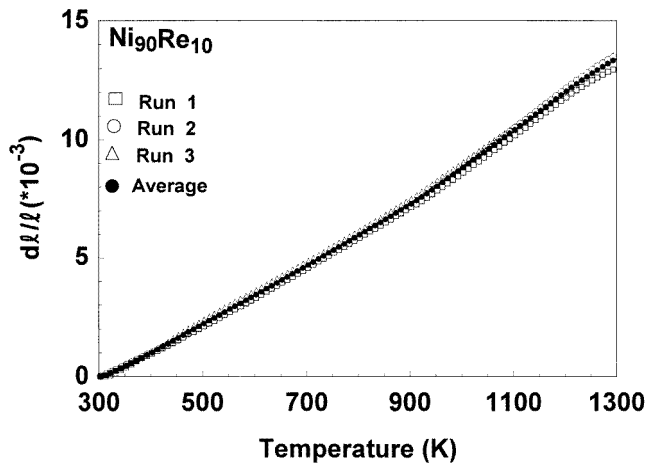

Figure 3. Measured $d\ell/\ell$ against temperature for $Ni_{90}Re_{10}$ alloy, showing the results of three separate measurements and their average.

In figure 3, we show the results of three experimental runs of $d\ell/\ell$ against temperature measurements for the $Ni_{90}Re_{10}$ alloy. For all the measurements presented here, results are based on the average of three similar experimental runs. In figure 4, we show $d\ell/\ell$ so determined against temperature for Ni and for $Ni_{100-x}Re_x$ alloys for $x = 5, 8, 10, 12, 16$
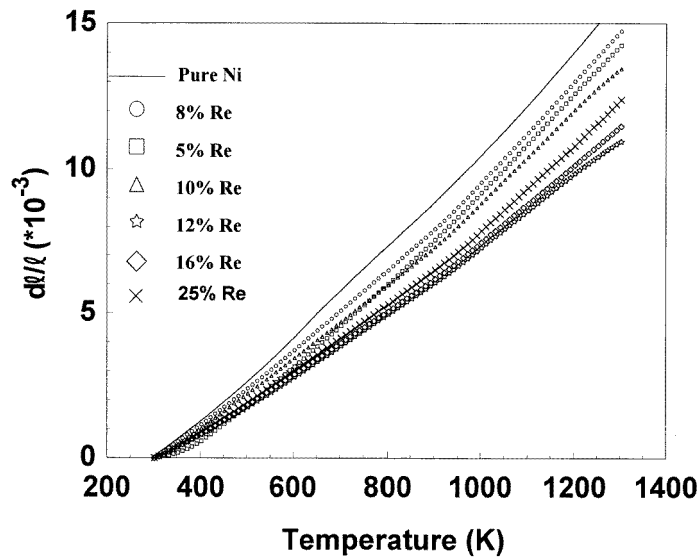
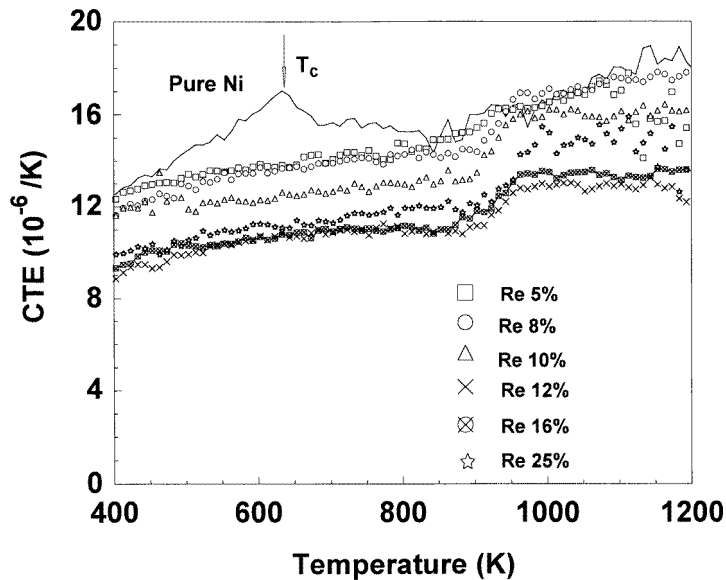**Figure 4.** Measured $d\ell/\ell$ against temperature for $Ni_{100-x}Re_x$ alloys, with x values noted on the graph.

Figure 5. The computed coefficient of thermal expansion against temperature for $Ni_{100-x}Re_x$ alloys.

and 25%. The computed values of the coefficients of thermal expansion, $\alpha = (1/l)(dl/dT)$, using this procedure and the data of average $d\ell/\ell$ against temperature, are estimated to be accurate to within $\pm 4\%$. The computed values of α from the data of figure 4 are shown in figure 5. For pure Ni, the peak in α at $T_c \simeq 630$ K is clearly evident and this anomaly has been discussed in great detail by Kollie. For the sample with $x = 5\%$, $T_c \simeq 350$ K (Babu

et al 1996) and the data for $T < 400$ K for this sample is therefore affected by magnetic ordering. For other samples, $T_c < 300$ K (Babu *et al* 1996) and a meaningful comparison can be made with the predictions of the molecular dynamics simulations.

In the results presented in figure 5, it is evident that the magnitude of α is lowest for the sample with $x = 12\%$. Thus, this minimum may be somehow associated with the fact that for $x \geqslant 12\%$, we have a two-phase system and that the different values of α for the two phases may tend to increase the measured α because of stresses produced at the boundaries of the two incompatible phases. It is perhaps fortuitous that T_c for Ni-base fcc alloys also goes to zero near $x \simeq 12\%$ (Besnus *et al* 1972, Gregory and Moody 1975, Kaiser and Smith 1989, Babu *et al* 1996). It is expected that magnetic contributions to α above room temperature will be negligible if T_c is at cryogenic temperatures.

The variations of α with the composition parameter x for $Ni_{1-x}Re_x$ alloys are shown in figure 6 for temperatures of 503, 903 and 1203 K. We have included the data for $x = 12$, 16 and 25% also, although it should be noted that these samples are two-phase materials, containing Re as the second phase and consequently the results of the simulations do not apply to these samples. Therefore, for comparison with the simulations, we only consider the results for $x \leqslant 10\%$ shown in figure 7. It is evident from figure 7 that at 1203 K, CTE is essentially independent of x in agreement with the predictions of Mei *et al* (1994). At lower temperatures, CTE decreases with increases in x, qualitatively similar to our observations for the NiCr and NiMo systems (Pavlovic *et al* 1996). The results of the molecular dynamics simulations for $Ni_{1-x}Re_x$ alloys, however, predict an increase in CTE with increases in x near room temperature (Mei *et al* 1994). An explanation for this discrepancy may in part be due to the unusual microstructure of NiRe alloys as discussed later.
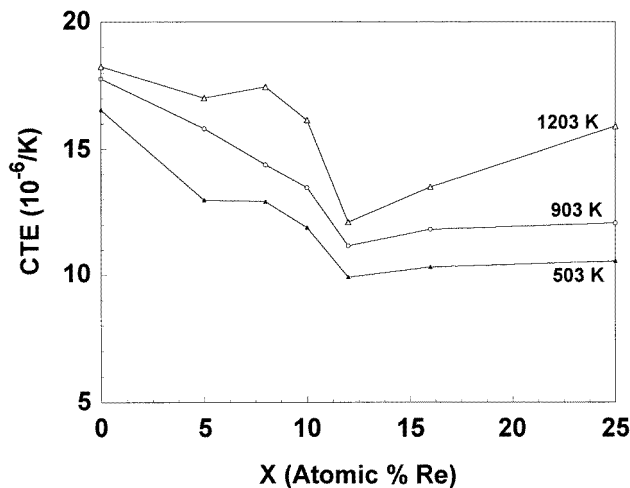

Figure 6. The coefficient of thermal expansion against x for $Ni_{100-x}Re_x$ alloys at selected temperatures of 503, 903 and 1203 K. Lines connecting the points are for visual aid.

In figure 8, we compare the grain structures of $Ni_{84}Cr_{16}$, $Ni_{95}Re_5$ and $Ni_{90}Mo_{10}$ alloys using optical micrographs. The dendrite-like small grain size in the NiRe alloy is clearly evident. This small and unusual grain size is expected to enhance shear stresses between grains in the NiRe system. Since the effect of applied pressure or stress is to lower the expansivity of a material (see e.g. Touloukian *et al* 1975), this may result in lower measured α for the NiRe system. In figure 5, we observe a rapid increase in α above 900 K for
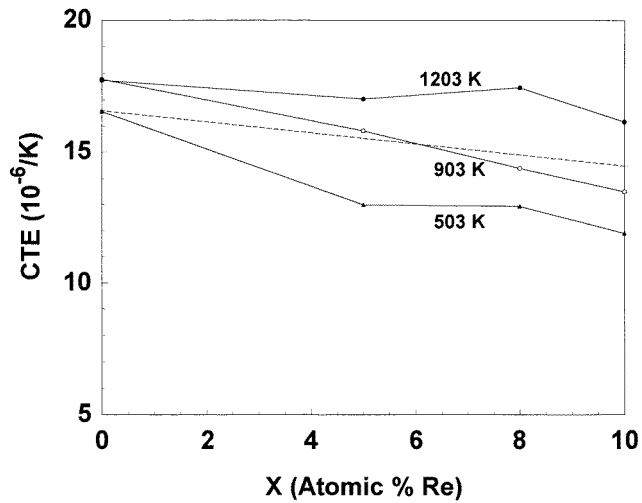
Figure 7. The coefficient of thermal expansion against x for single phase $Ni_{100-x}Re_x$ for $x \leqslant 10\%$ at three temperatures. The broken curve is the calculated curve using equation (1) with parameters given in the text.
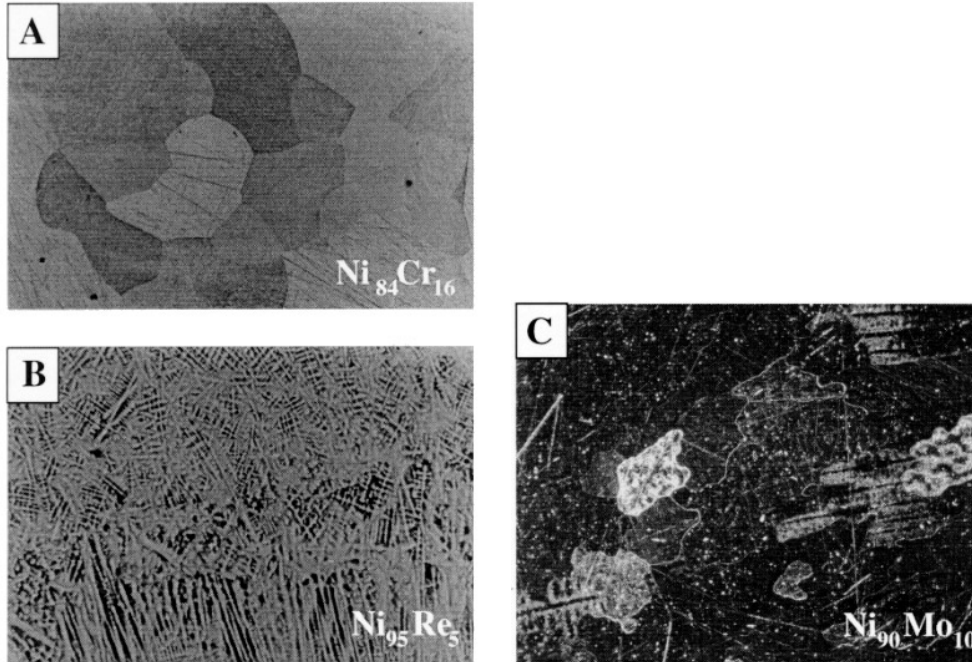

Figure 8. Room temperature optical micrographs ($50\times$ magnifications) of $Ni_{84}Cr_{16}$, $Ni_{95}Re_5$ and $Ni_{90}Mo_{10}$ (dark field) alloys, showing denderitic grain structure for the NiRe system.

the NiRe system, the effect becoming more pronounced as Re concentration increases. In contrast, no such increase is observed for the pure Ni system. It is possible that this increase in α above 900 K is due to thermal relaxation of shear stresses at grain boundaries

leading to a sudden increase in α. Once these stresses are released, α resumes its normal temperature variation. Although our samples were annealed at 1273 K for 120 h in argon prior to measurements (Pavlovic *et al* 1996) this does not eliminate the intergrain stresses once the samples are cooled to room temperature. If this argument is valid, then for the NiRe system, a meaningful comparison of the experimental results with theoretical/modelling predictions is not possible for data below about 1000 K unless the grain size is significantly increased by improved metallurgy.

The expansivity of a binary alloy (see e.g. Touloukian *et al* 1975) in which thermal shear stresses are negligible, can be written as

$$\alpha = \frac{\alpha_1 B_1 V_1 (1-x) + \alpha_2 B_2 V_2 x}{B_1 V_1 (1-x) + B_2 V_2 x} \tag{1}$$

where α_i, B_i and V_i are respectively the expansivity, bulk modulus and fractional volume of atoms for the two elements of the alloy. For $Ni_{1-x}Re_x$ alloys, we use the following room temperature values (Touloukian *et al* 1975, Pavlovic *et al* 1996) for Ni and Re respectively: $\alpha = 13.4$ (Ni) and 6.2 (Re) in units of 10^{-6} K^{-1}; $B = 1.86$ (Ni) and 3.72 (Re) in units of 10^{12} dynes cm^{-2}; $V = 10.935$ A^3 (Ni) and 14.572 A^3 (Re). The calculated curve using equation (1) and these values is shown in figure 7 as the broken curve. The slope of this curve coincides with that of the data at 1203 K whereas the slopes for the data at 503 and 903 K are considerably higher. The limitations for the use of equation (1) is that we have used room temperature values for the parameters since the high-temperature values of B and V are not known. However, the larger values of B and V and the smaller value of α for Re (relative to Ni) are not likely to change with temperature and, hence, the trend predicted by equation (1) should still be valid.

In summary, the results presented here for $Ni_{100-x}Re_x$ alloys show that for $x \leqslant 10\%$, Re enters substitutionally for Ni in the fcc structure with increased lattice constant. For these stable fcc alloys, CTE above 1000 K is only weakly dependent on x, in agreement with the predictions from molecular dynamics simulations and also equation (1). It is argued that measurements in NiRe alloys below 1000 K are affected by the shear stresses present in the denderitic grain structure of these alloys, making an unambiguous comparison difficult. For the two-phase alloys with $x \geqslant 12\%$, a minimum in CTE occurs at $x = 12\%$ at all temperatures. This result may have practical implications for producing alloys with low CTE.

Acknowledgments

References

Babu V Suresh, Pavlovic A S and Seehra M S 1996 *J. Appl. Phys.* **79** 5230
Besnus M J, Gottehrer Y and Munschy G 1972 *Phys. Status Solidi* **49** 597
Bradley E F (ed) 1988 *Superalloys* (Metals Park, OH: ASM International)
Gregory I P and Moody D E 1975 *J. Phys. F: Met. Phys.* **5** 36
Kaiser A B and Smith T F 1989 *Physica* B **160** 33
Kollie T G 1977 *Phys. Rev.* B **16** 4872
McNallan M J, Lee Y Y, Chang Y W, Jacobson N S and Doychak J 1991 *J. Electrochem. Soc.* **138** 3692

Mei J, Cooper B R, Hao Y G and VanScoy F L 1994 *Alloy Modeling and Design* ed G M Stocks and P E A Turchi
    (Warrendale, PA: TMS Publishing) pp 165–74
Mukherjee G D, Bansal C and Chatterjee A 1996 *Phys. Rev. Lett.* **76** 1876 and reference therein
Nash A and Nash P 1985 *Bull. Alloy Phase Diagram* **6** 348
Okamoto H 1991 *J. Phase Equilibria* **12** 623
Pavlovic A S, Babu V Suresh and Seehra M S 1996 *J. Phys.: Condens. Matter* **8** 3139
Touloukian Y S, Kirby R K, Taylor R E and Desai P D 1975 *Thermophysical Properties of Matter* vol 12 (New York:
    Plenum)