Journal of Alloys and Compounds 281 (1998) 237–240

Journal of
ALLOYS
AND COMPOUNDS

Investigation of the short-range order in Au–Te melts

Abeer Yassin[a], Robert Castanet[b,*]

[a]Department of Physics, University of Baghdad, Al-Jadriyah, Baghdad, Iraq

[b]Centre de Thermodynamique et de Microcalorimetrie du CNRS, 26 rue du 141eme R.I.A., F-13003, Marseille, France

Received 25 June 1998

Keywords: Enthalpy; Entropy; Heat capacity; Short-range order; Au–Te liquid alloys

1. Introduction

The phase diagram of the Au–Te binary system is well-known as shown in Fig. 1 [1]. It shows one intermediate compound, $AuTe_2$, which does not correspond to the normal valencies of the components. In contrast, the congruently melting compounds of the Cu–Te and Ag–Te binaries (Cu_2Te and Ag_2Te) obey the valencies of the components.

In three previous papers, we reported the results of the enthalpy of formation [2] and of free enthalpy of formation [3] of the Au–Te melts with respect to temperature and composition and the heat contents versus temperature of four alloys corresponding to the two eutectics of the system ($x_{Te}=0.88$ and 0.53) as well as the two-phase regions ($x_{Te}=0.60$ and 0.77) [4]. In a previous paper, Anrès et al. [5] also reported the data corresponding to the heat content of the intermediate compound.

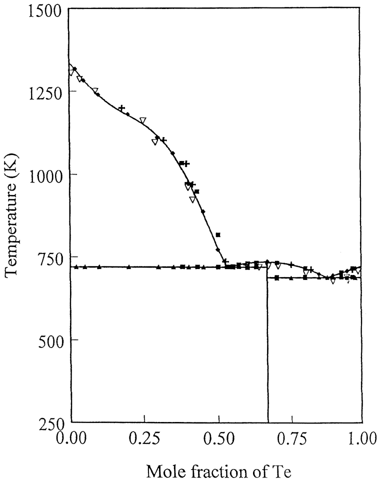

Fig. 1. Phase diagram of the Au–Te binary according to Moffatt [1].

The enthalpy of formation of the melts is slightly negative on the Te-rich side and becomes positive on the Au-rich side. There are two regions in which the enthalpy of formation of the liquid does not depend on temperature but in a narrow temperature range the enthalpy of formation of the melt undergoes a sudden jump corresponding to an increase of enthalpy with increasing temperature. When the enthalpy of formation of the melts is strongly negative, such a jump can be attributed to the destruction of some short-range order by thermal agitation [6]. It does not seem to be the case here and the aim of this paper is to try to explain the unusual behaviour of the Au–Te melts.

2. Thermodynamic behaviour of the Au–Te melts

In the investigated range, the two temperature regions in which the enthalpy of formation can be assumed temperature independent are 737–819 K (called low-temperature region, LT) and 872–1000 K (called high-temperature region, HT). In the first one, we found $h^{f}_{min}=-1098$ J mol^{-1} for $x_{Te}=0.63$. In the second one, $h^{f}_{min}=-628$ J mol^{-1} for $x_{Te}=0.69$ (Fig. 2). The increase in enthalpy between 819 and 872 K (Fig. 3) leads to positive excess heat capacity values in the Te-rich side. For $x_{Te}=0.667$, C^{xs}_{P} is at least 8.7 J K^{-1} mol^{-1} if we assume that the transition begins at 819 and ends at 872 K. The sign of C^{xs}_{P} in the Au-rich side cannot be determined since we did not perform any measurement in this domain of composition.

From our free enthalpy of formation data combined with our enthalpy of formation results, we calculated the entropy of formation of the melt at 753 K as shown on Fig. 4. The curve shows clearly a tendency to give a minimum near the composition of the intermediate compound.

---

*Corresponding author.

0925-8388/98/$ – see front matter

PII: S0925-8388(98)00786-5

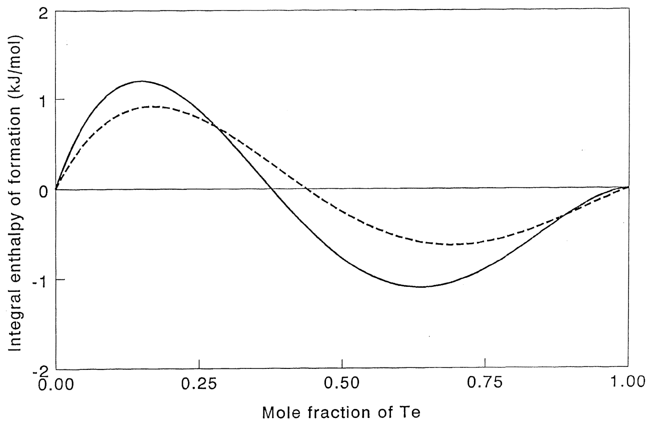

Fig. 2. Molar integral enthalpy of formation of the Au–Te melts versus mole fraction of Te according to [2]. ———: Low temperature (LT): – – – – – –: High temperature (HT).

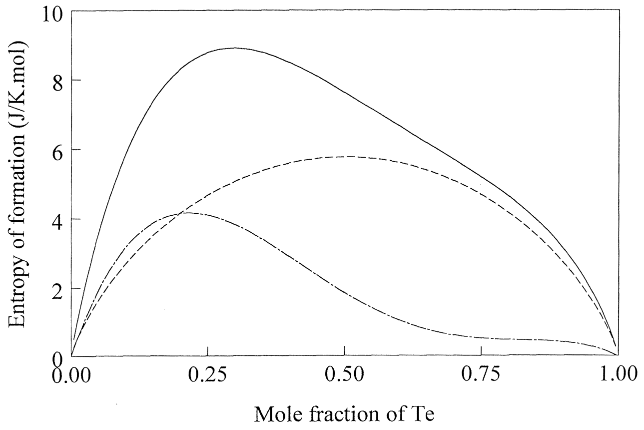

Fig. 4. Molar integral entropy of formation of the Au–Te liquid alloys versus mole fraction of Te at 753 K. ———: Entropy of formation, — — — — —: Excess entropy of formation – – – –: Ideal entropy of formation.

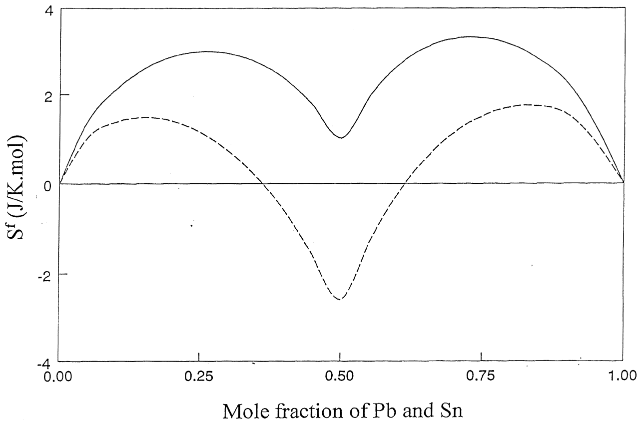

Fig. 5. Molar integral entropy of formation of the Sn–Te (– – –) and Pb–Te (———) melts according to the regular associated solution model [9].

3. Discussion

It is well known [7] that the integral entropy of mixing of an associated solution shows a minimum corresponding to the stoichiometry of the associates. We observed such a behaviour in many binary systems as for example the Sn–Te and Pb–Te alloys [8]. Their entropies of mixing show very strong minima at the composition corresponding to the SnTe and PbTe intermediate compounds (Fig. 5). Moreover, in the case of the Sn–Te melts the minimum of the configurational entropy ($x_{sn}=0.5$) is very close to zero due to the fact that the liquid is completely associated at this composition. Such minima disappear at high temperature due to the destruction of the associates by thermal agitation.

In the case of the Au–Te melts, the same behaviour is observed but their enthalpy of formation does not seem to be negative enough to assume the existence of associates. However, we tried to apply the regular associated solution model [9] to the system. The thermodynamic functions of formation of the melts obtained from our previous experimental investigations [2,3], i.e. the integral enthalpy and free enthalpy of formation, were used for such a purpose. The model of regular associated solutions employed to describe the thermodynamic behaviour of the melt is based on the assumptions of Bhatia and Hargrove

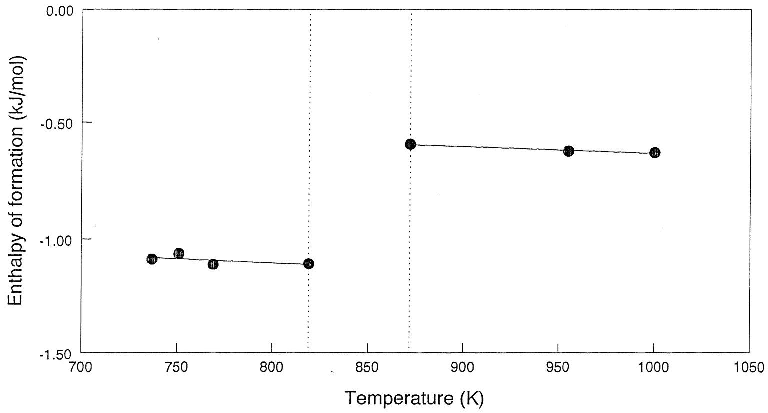

Fig. 3. Molar integral enthalpy of formation of the Au–Te liquid alloys versus temperature for $x_{Te}=0.65$ according to [2].

[10]. The binary melt is considered as a ternary one (free Au atoms, free Te atoms and Au_aTe_b associations). Then, the thermodynamic functions of formation of the liquid alloy are assumed to be due mainly to the formation of the associates with additional contributions from the interactions between the three species. We used two expressions for the definition of the configurational entropy [9] taking into account the difference in volume of free atoms and associates. The first one (S_1) corresponds to a quasi-lattice model with frozen sites on which monoatomic species (Au and Te) cannot be exchanged with atoms in heteroatomic species (Au_aTe_b). For the second one (S_2), any exchange between free atoms and Au and Te atoms in the associates is allowed. We made three assumptions about the stoichiometry of the Au_aTe_b associates: AuTe, $AuTe_2$ which is that of the only intermediate compound and Au_2Te which corresponds to the normal valencies of the components as for the Cu–Te and Ag–Te similar systems.

The fit obtained assuming AuTe associates was very poor whatever the definition of the configurational entropy and whatever the number of interaction parameters used for the calculation. The calculated data assuming $AuTe_2$ associates differ strongly from the experimental ones on the Te-rich part for the enthalpy of formation whatever the definition of S_{conf} as shown as an example in Fig. 6 (S_2). Finally, the best fit was obtained when the calculation was performed assuming Au_2Te associates and the Flory (S_2) definition of the configurational entropy. As shown in Figs. 7 and 8, the agreement between calculated and experimental data of the enthalpy and free enthalpy of formation of the melts is good enough to assume Au_2Te species taking into account $Au–Au_2Te$ and $Te–Au_2Te$ interactions. We obtained $\Delta H_0=-3.45$ kJ mol^{-1} and $\Delta S_0=6.3$ J.K^{-1} mol^{-1}, $\omega(Au–Au_2Te)=-13.1$ kJ mol^{-1} and $\omega(Te–Au_2Te)=-7.7$ kJ mol^{-1} in this manner where ΔH_0 and ΔS_0 are the standard enthalpy and entropy of formation of the associates respectively and ω_i, are the interaction parameters.

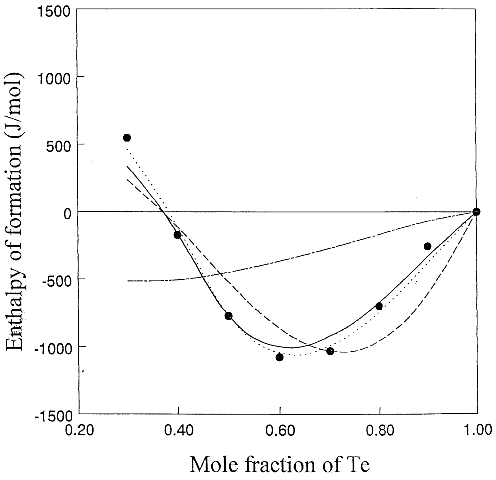

Fig. 7. Molar integral enthalpy of formation of the Au–Te melts at low temperature. Experimental solid circles; Calculated according to the regular associated solution model assuming Au_2Te associated species, the S_2 definition for the configurational entropy and no interaction parameters (— — — –), one interaction parameter (Au/Te, – – – –), two interaction parameters (Au/Au_2Te and Te/Au_2Te, – – – – – –) and three interaction parameters (Au/Te, Au/Au_2Te and Te/Au_2Te, ———).

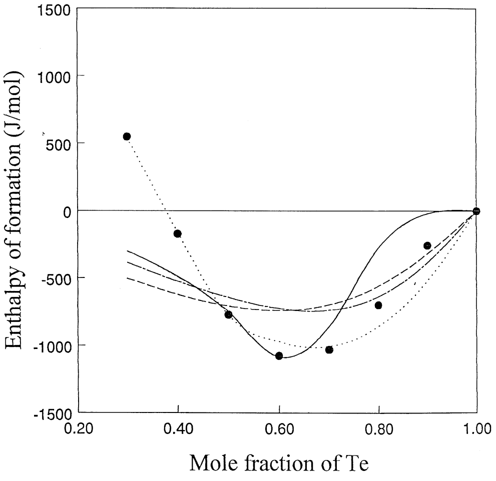

Fig. 6. Molar integral enthalpy of formation of the Au–Te melts at low temperature. Experimental solid circles; Calculated according to the regular associated solution model assuming $AuTe_2$ associated species, the S_2 definition for the configurational entropy and no interaction parameters (— — — –), one interaction parameter (Au/Te, – – –), two interaction parameters ($AuIAuTe_2$ and $Te/AuTe_2$, – – – – – –) and three interaction parameters (Au/Te, $Au/AuTe_2$ and $Te/AuTe_2$, ———).

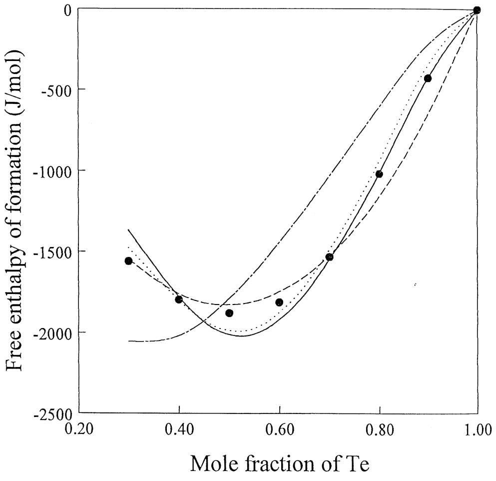

Fig. 8. Molar integral free enthalpy of formation of the Au–Te melts at low temperature. Experimental solid circles; Calculated according to the regular associated solution model assuming Au_2Te associated species, the S_2 definition for the configurational entropy and no interaction parameters (— — — –), one interaction parameter (Au/Te, – – –), two interaction parameters (Au/Au_2Te and Te/Au_2Te, – – – – – –) and three interaction parameters (Au/Te, Au/Au_2Te and Te/Au_2Te, ———).

4. Conclusion

The application of the model leads to the conclusion that the thermodynamic behaviour of the Au–Te melts can be explained partly by the existence of Au_2Te associates. Thus, the short-range order in the liquid obeys the normal valencies of the components, as for the CuTe and Ag–Te binaries, although the only intermediate compound of the system is $AuTe_2$. However, it has to be pointed out that we did not take into account in our fitting the thermodynamic data on the Au-rich melts since they are extrapolated. In the Au-rich region, the enthalpy of formation is undoubtedly too positive to be assumed in the framework of the model. Moreover, the standard enthalpy of formation of the Au_2Te species is very weakly negative (-3.45 kJ mol^{-1}) and the residual contributions due to interactions between associates and free atoms are negative. Therefore, it is necessary to assume that two phenomena act together in the liquid. The first one, whose contribution to the enthalpy of formation is negative, is the short-range order based on Au_2Te stoichiometry. The second one, whose contribution is positive, should be due to the modification of the equilibrium between two forms of Te. Thus, the melt has to be considered as a quaternary system which could explain that its entropy of formation is larger than the ideal entropy of mixing calculated assuming a ternary system. Indeed, Bellissent et al. [11,12] showed that the connectivity of tellurium increases from 2 to 3 when the temperature increases. The $Te^{II} \rightarrow Te^{III}$ equilibrium is obviously modified not only by the temperature but also by the concentration of gold. Amzil et al. [13] were able to explain the thermodynamic behaviour of Se–Te melts in this manner. When this positive contribution is taken into account, the negative part due to the associations should lead to a larger negative value of the standard enthalpy of formation of the associates. For such a purpose, a more sophisticated model has to be developed in which four species (Au, Te^{II}, Te^{III} and Au_aTe_b) should be assumed.

References

[1] W. Moffatt, Handbook of Binary Phase Diagrams, Genium Pub. Corp., Schenectady, NY, USA, 1987.

[2] A. Yassin, R. Castanet, J. Alloys Comp. 252 (1997) 162.

[3] A. Yassin, R. Chastel, R. Castanet, Phys. Chem. Liquids 34 (1997) 65.

[4] A. Yassin, R. Castanet, High Temp. Mater. Processes 163 (1997) 201.

[5] P. Anrès, H. Bros, A. Coulet, R. Castanet, Phys. Chem. Liquids 28 (1994) 63.

[6] R. Castanet, Anal. Fisica, B 86 (1990) 129.

[7] R. Castanet, M. Gilbert, J.-C. Mathieu, J. Less-Common Met. 96 (1984) 1.

[8] R. Castanet, Z. Metallkde 80 (1989) 737.

[9] C. Bergman, R. Castanet, H. Said, M. Gilbert, J.-C. Mathieu, J. Less-Common Met. 85 (1982) 121.

[10] A.B. Bhatia, W.H. Hargrove, Phys. Rev. B 10 (1974) 3186.

[11] R. Bellissent, A. Menelle, A.M. Flank, Europhys. Lett. 4 (1987) 705.

[12] R. Bellissent, A. Menelle, A.M. Flank, Physica B 156–157 (1989) 174.

[13] A. Amzil, C. Bichara, R. Castanet, J.-C. Mathieu, Calphad XXV, Erice (Italy), 1996.