

Miedema模型在含O和S熔体与合金中的扩展与应用*

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摘要 将Miedema模型与实验数据相结合得到适于Miedema模型的O和S的参数(O: 电负性7.04、电子密度6.03、摩尔体积4.59; S: 电负性5.8、电子密度3.24、摩尔体积6.97), 计算了141种O的二元化合物和145种S的二元化合物生成焓其平均绝对误差(MAPE)分别为36.8%、32.4%。结合Ding导出的三元系相互作用系数计算模型, 计算了1873 K时Fe基熔体中O和S与其它元素之间的相互作用系数。与实验数据的比较表明, 除个别元素外, 计算值与实验值之间误差不大且变化趋势比较一致。将误差较大的Nb、Ag、Pt的电负性参数由原来的4.05、4.35、5.65修正为4.31、4.17、5.57, 使用Miedema模型的计算精度有很大的提高。

关键词 材料科学基础学科, Miedema模型, 含O和S熔体与合金, 相互作用系数, 参数的修正

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Extension and Application of Miedema's Model in O and S Containing Melts and Alloys

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ABSTRACT Combined Miedema's model with experimental data provided by Kleppa, the parameters of oxygen and sulfur which were satisfied with Miedema's model were derived: Oxygen: electronegativity 7.04, electronic density 6.03, molar volume 4.59; Sulfur: electronegativity 5.8, electronic density 3.24, and molar volume 6.97. In comparison with results from literature, those parameters had been turned out to be highly reasonable to Miedema's model. The mean absolute percentage error of enthalpies of formation of binary alloying oxides and sulfides were 36.8%, 34.2% respectively. Combining Ding's model, the activities and interaction coefficients between oxygen and other elements of Fe-based alloying melt in 1873 K were derived and further compared with available experimental data. Calculated results were confirmed to be in good agreement with available experimental data, except some special cases. Therefore the long-term problem related with the parameters of oxygen and sulfur for Miedema's model has been resolved successfully by this method. In particular, the special cases Nb, Pt, Ag-their electronegativities (4.05, 5.65, 4.35) were revised to be 4.31, 5.57 and 4.17, respectively, and the revised parameters were much more reasonable than the original parameters.

KEY WORDS foundational discipline in materials science, Miedema's model, oxygen and sulfur containing melts and alloys, interaction coefficients, revision of parameters

冶金熔体中的O和S含量的精确控制, 一直困扰着冶金工作者^[1-3]。在冶金凝固过程中O和S发生偏析, 形成具有严重危害的氧化物、硫化物夹杂等, 对成品的弯曲性、延展性、韧性和焊接性等都有

不利的影响。因此, O和S含量的控制是生产特殊钢及高新材料的首要任务^[4]。为了控制O和S的含量, 必须知道其在熔体中的热力学行为及热力学参数。用实验手段可得到O和S的热力学参数, 但是较多的影响因素限制了高温实验结果的使用^[5]。Ding曾将Miedema模型与其他热力学模型相结合给出了二元及三元高温熔体中组元相互作用系数

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的计算公式^[6,7],并对Fe-Cu和Co-基三元体系元素之间的相互作用系数进行了详细的计算。但是,Miedema模型没有给出O和S的计算模型参数,不能计算许多含O和S的体系。O族元素不能形成假想的金属态且可转移的电子较少,因此Miedema等认为该模型对O族元素不适用^[8]。

本文将实验数值与Miedema模型相结合^[9],计算适于Miedema模型的O和S参数,并进行对比^[10]。为了验证所得的结果,将其代入活度系数计算模型^[6,7]中,计算1873 K时Fe基熔体中O和S与其它元素之间的相互作用系数,并与实验值^[11]比较。

1 O和S参数获取的研究方法

Chen^[9]研究Zr基合金时发现,Miedema模型计算结果与实验数据差距较大。因此提出了将实验室数据、第一原理计算与Miedema模型相结合的方式将Zr的电负性参数由3.45修正为3.62,修正后的数据使Miedema模型的计算精度有了很大提高。基于此,本文将以Miedema模型与实验数据相结合的方式计算O和S的参数,方法如下:

(a) 收集尽可能多的O和S与其它元素形成化合物生成焓的实验值 ΔH_{exp} 。

(b) 根据元素的周期性给出O和S的参数(电子密度,电负性,摩尔体积)初始值。 ΔH_{exp} 与Miedema模型相结合,改变一参数同时对另外两参数不断修正不断优化参数,以使得到的结果为最佳MAPE (Mean Absolute Percentage Error)值,并与Sun计算的数据比较^[12]。MAPE的计算公式

$$\text{MAPE} = \frac{1}{N} \sum_{i=1}^N \left| \frac{y_i - t_i}{t_i} \right| \times 100\% \quad (1)$$

式中 N 为所有化合物的个数, y_i 为对应的计算数据, t_i 为实验数据。

Miedema模型的计算公式^[13]为

$$\Delta H_{\text{Mie}} = f_B^A \frac{2x_A V_A^{2/3} \left\{ -P(\phi_A^* - \phi_B^*)^2 + Q \left((n_{\text{ws}}^{1/3})_A - (n_{\text{ws}}^{1/3})_B \right)^2 - R \right\}}{(n_{\text{ws}}^{1/3})_A^{-1} + (n_{\text{ws}}^{1/3})_B^{-1}} \quad (2)$$

式中 P 、 Q 、 R 为经验常数, n_{ws} 、 ϕ^* 、 V 为边界电子密度、电负性、摩尔体积。

(c) 得到最优的参数值,代入Ding^[6,7]导出的相互作用系数计算公式计算1873 K时Fe基熔体中O和S与其它元素之间的相互作用系数,并与实验值进行比较。

(d) 将实验数据与Miedema模型相结合,对研究过程中出现误差较大的元素参数进行再修正。

2 O和S参数的获得及对结果的分析

2.1 O参数的获得及结果分析

由于Miedema模型对过渡元素计算精度较高,本文先研究101个过渡元素氧化物体系,以期得到最佳的MAPE值。得到O的参数为: $\phi^* = 7.04$ 、 $n_{\text{ws}}^{1/3} = 1.82$ 、 $V^{2/3} = 2.76$ 、 $r = 2.5$ 、 $\mu = 0.04$,如图1所示。

图1中的实线表示实验值与计算值100%符合,虚线表示为 $\Delta H_{\text{exp}} \pm 50$ kJ/mol-atom变化范围。实心点表示本文的计算结果,半填充点为文献^[10]($\phi^* = 6.97$ 、 $n_{\text{ws}}^{1/3} = 1.70$ 、 $V^{2/3} = 2.66$ 、 $r = 2.45$ 、 $\mu = 0.04$)结果。通过实验数据与Miedema模型不断拟合得到O的参数为: $\phi^* = 7.04$ 、 $n_{\text{ws}}^{1/3} = 1.82$ 、 $V^{2/3} = 2.76$ 、 $r = 2.5$ 、 $\mu = 0.04$ 。在图中可见大部分点落在实线 ± 50 kJ/mol-atom的变化范围之内,但总体来说实验值与计算值之间的误差还比较大。尤其是生成焓的实验值越小,计算值与实验值的波动就越大。误差较大的有碱土元素的过氧化物(CaO_2 、 BaO_2 、 SrO_2),第一副族元素的氧化物(CuO 、 Cu_2O 、 Ag_2O 、 Au_2O_3),贵金属的氧化物(PdO 、 Pt_2O_3 、 RhO 、 Rh_2O_3)。由于过氧键的结构复杂,其化合物生成焓不可能通过简单的模型计算就能获得。对其它化合物,与文献中查的数据进行比较可以看出本文的结果与文献中计算结果还是比较符合的,较大的波动是模型的精度造成的。这说明,Miedema模型还需要进一步修正和改进^[14,15]。表1列出了对142个过渡元素、非过渡元素与氧形成化合物生成焓的计算结果与实验值^[8,10,16,17]的比较。从表中可见,若按照符号一致率的要求,计算的结果符号100%与实验值相同。表中个别的如 Ag_2O 生成焓的实验值为-10.35 kJ/mol-atom,与模型计算值-101.99 kJ/mol-atom有很大的差别,故将此类化合物另行处理。对141个化合物计算

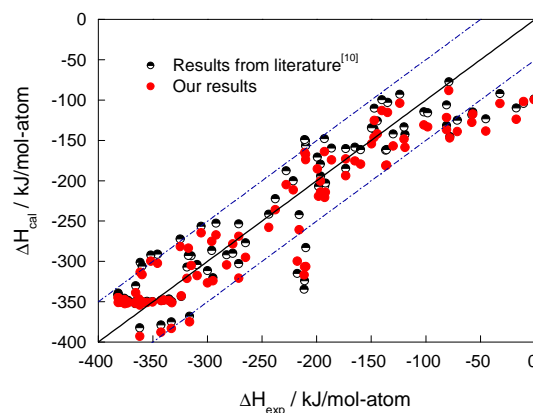


图1 过渡元素氧化物生成焓实验值与计算值的比较
Fig.1 Comparison between experimental and calculated enthalpies of formation of transition oxides

表 1 氧化物生成焓的结果比较
Table 1 Comparison of enthalpies of formation of oxides (kJ/mol-atom)

Comp	ΔH_{exp}	ΔH_{cal}	$\Delta H_{\text{lit}}^{[10]}$	Comp	ΔH_{exp}	ΔH_{cal}	$\Delta H_{\text{lit}}^{[10]}$
Sc ₂ O ₃	-381.764	-345.005	-341.329	CeO ₂	-362.889	-346.538	-348.575
Y ₂ O ₃	-355.439	-350.970	-349.580	Ce ₂ O ₃	-359.238	-351.035	-350.514
La ₂ O ₃	-358.740	-350.775	-350.702	CeO _{1.72}	-366.048	-351.863	-352.526
TiO	-271.332	-320.792	-302.888	CeO _{1.83}	-364.993	-350.472	-351.696
TiO ₂	-314.916	-305.285	-293.060	Pr ₂ O ₃	-361.931	-392.932	-382.518
Ti ₂ O ₃	-300.026	-326.757	-311.466	Pr ₇ O ₁₂	-342.632	-387.898	-378.967
Ti ₃ O ₅	-318.643	-321.200	-306.972	PrO _{1.833}	-333.066	-383.199	-375.059
Ti ₄ O ₇	-309.502	-317.685	-303.979	PrO ₂	-316.450	-375.025	-367.933
ZrO ₂	-365.821	-338.979	-330.139	Nd ₂ O ₃	-361.581	-350.593	-349.672
HfO ₂	-381.581	-351.037	-339.316	Sm ₂ O ₃	-364.728	-351.412	-349.987
VO	-215.895	-261.029	-241.936	Eu ₂ O ₃	-332.544	-351.265	-349.852
V ₂ O ₃	-243.760	-258.008	-241.508	EuO	-295.00	-324.117	-320.167
V ₂ O ₄	-237.860	-236.011	-222.423	Gd ₂ O ₃	-365.380	-350.970	-349.580
V ₂ O ₅	-221.513	-211.273	-200.009	TbO _{1.72}	-350.410	-350.455	-349.799
NbO	-209.827	-306.656	-283.019	TbO _{1.81}	-342.314	-348.633	-348.452
NbO ₂	-264.987	-295.157	-276.932	TbO _{1.83}	-339.958	-348.142	-348.064
Nb ₂ O ₅	-271.362	-268.916	-253.588	TbO ₂	-323.842	-342.916	-343.665
Ta ₂ O ₅	-292.282	-267.213	-252.517	Tb ₂ O ₃	-373.045	-351.597	-349.714
CrO ₂	-199.298	-185.376	-170.951	Ho ₂ O ₃	-376.142	-347.335	-345.757
CrO ₃	-147.382	-146.466	-135.999	Tm ₂ O ₃	-377.732	-349.348	-347.184
Cr ₂ O ₃	-227.940	-204.957	-187.777	Yb ₂ O ₃	-335.159	-348.651	-346.538
MoO ₂	-196.313	-214.030	-194.366	Lu ₂ O ₃	-375.640	-352.388	-349.560
MoO ₃	-186.272	-174.241	-159.528	CaO	-317.544	-283.597	-292.851
WO ₂	-196.564	-200.640	-179.461	CaO ₂	-217.568	-299.816	-314.971
WO _{2.72}	-209.987	-173.865	-156.530	SrO	-296.018	-275.276	-286.468
WO _{2.9}	-210.273	-167.435	-150.915	SrO ₂	-211.153	-306.869	-324.179
WO _{2.96}	-210.848	-165.346	-149.085	Dy ₂ O ₃	-372.620	-350.333	-348.545
WO ₃	-192.883	-163.970	-147.877	Er ₂ O ₃	-379.572	-350.715	-348.450
MnO	-192.611	-220.677	-206.763	Pt ₂ O ₃	-17.200	-123.888	-109.852
Mn ₂ O	-173.343	-172.952	-160.001	Pm ₂ O ₃	-362.00	-354.350	-352.716
Mn ₂ O ₃	-191.800	-214.350	-202.843	Al ₂ O ₃	-335.138	-133.255	-135.980
Mn ₃ O ₄	-198.257	-219.218	-206.851	Li ₂ O	-199.577	-144.818	-150.632
MnO ₂	-173.343	-193.831	-184.631	Li ₂ O ₂	-158.155	-185.273	-195.531
MnO _{3.5}	-81.009	-136.888	-131.518	NaO ₂	-86.888	-150.244	-168.986
TcO ₂	-144.348	-142.045	-125.833	Na ₂ O	-139.327	-111.831	-121.998
ReO ₂	-149.648	-154.220	-134.557	K ₂ O	-120.499	-101.843	-113.543
ReO ₃	-147.277	-125.425	-110.314	K ₂ O ₂	-123.846	-148.310	-165.773
Re ₂ O ₇	-140.350	-113.029	-99.633	RbO ₂	-92.885	-165.548	-188.489

续表 1

Comp	ΔH_{exp}	ΔH_{cal}	$\Delta H_{\text{lit}}^{[10]}$	Comp	ΔH_{exp}	ΔH_{cal}	$\Delta H_{\text{lit}}^{[10]}$
Fe _{0.947} O	-136.759	-181.379	-162.284	Rb ₂ O	-113.0	-99.418	-111.251
FeO	-136.022	-180.635	-161.407	RbO	-102.500	-145.340	-162.871
Fe ₂ O ₃	-164.850	-175.606	-158.481	Rb ₂ O ₃	-105	-164.494	-185.603
Fe ₃ O ₄	-159.769	-179.547	-161.570	CsO ₂	-95.395	-165.765	-188.838
RuO ₂	-101.671	-130.929	-114.703	Cs ₂ O	-115.325	-96.347	-108.208
OsO ₂	-98.324	-133.493	-115.745	Cs ₂ O ₃	-104.014	-161.853	-182.874
OsO ₄	-78.820	-88.202	-77.356	BeO	-304.177	-70.594	-65.942
CoO	-118.972	-158.652	-142.658	MgO	-300.621	-177.756	-183.611
Co ₃ O ₄	-130.003	-156.938	-142.119	ZnO	-175.230	-124.300	-128.760
Rh ₂ O ₃	-71.128	-139.034	-124.998	CdO	-129.495	-117.887	-125.878
Rh ₂ O	-32.00	-104.419	-91.931	HgO	-45.395	-101.212	-110.577
RhO	-45.00	-138.666	-123.457	B ₂ O ₃	-254.387	-52.474	-46.710
IrO ₂	-80.891	-121.620	-106.023	Ga ₂ O ₃	-217.819	-133.261	-139.356
NiO	-119.851	-148.453	-133.407	In ₂ O ₃	-185.158	-127.937	-140.029
PdO	-57.739	-127.772	-118.532	Tl ₂ O	-56.345	-74.196	-82.719
CuO	-78.032	-146.924	-145.455	Tl ₂ O ₃	-78.910	-113.520	-128.458
Cu ₂ O	-56.902	-117.606	-114.807	SiO ₂	-291.977	-89.570	-90.912
Ag ₂ O	-10.350	-101.987	-104.071	GeO ₂	-193.301	-86.068	-92.797
Au ₂ O ₃	-0.669	-99.794	-98.720	SnO	-142.885	-110.728	-119.478
ThO ₂	-408.805	-369.414	-365.369	SnO ₂	-193.608	-118.285	-129.519
UO ₂	-361.633	-313.713	-301.150	PbO	-109.031	-91.065	-104.280
UO ₃	-305.746	-264.824	-256.586	PbO ₂	-91.490	-99.740	-115.816
U ₃ O ₈	-324.983	-281.594	-272.158	Pb ₂ O ₃	-98.340	-100.222	-115.600
U ₄ O ₉	-345.705	-302.423	-291.146	Pb ₃ O ₄	-102.669	-98.611	-113.466
PuO	-282.420	-304.615	-291.869	As ₂ O ₃	-130.959	-85.496	-90.205
PuO ₂	-351.944	-299.882	-292.039	As ₂ O ₅	-132.096	-75.370	-80.510
Pu ₂ O ₃	-359.824	-316.338	-305.879	Sb ₂ O ₃	-144.061	-94.780	-106.615
BaO	-276.772	-278.500	-289.899	Sb ₂ O ₄	-151.192	-93.831	-106.266
BaO ₂	-211.431	-316.987	-334.600	Sb ₂ O ₅	-138.843	-88.985	-101.335
Sc ₂ O ₃	-381.764	-345.005	-341.329	Bi ₂ O ₃	-114.776	-97.903	-113.273
La ₂ O ₃	-358.740	-350.775	-350.702	P ₂ O ₅	-214.995	-36.955	-36.338

其 MAPE 为 36.8%, 文献^[10]的数据计算 MAPE 值为 36.4%, 两者差距不大。通过与 Sun 计算其它化合物体系时所得的 37.3% 及 Lewis 推荐的 50% 比较^[12], 可以看出, 本文的结果可用于计算含 O 体系。

2.2 S 参数的获得及结果分析

用同样的方式研究 S 与过渡元素形成的化合物体系, 得到 S 的参数为: $\phi^* = 5.80$ 、 $n_{\text{ws}}^{1/3} = 1.48$ 、 $V^{2/3} = 3.65$ 、 $r = 2.5$ 、 $\mu = 0.04$ 。其生成焓计算值与实验值对

应的结果如图 2 所示。

图 2 给出了 97 个过渡元素硫化物生成焓的实验值与计算值的比较, 实心圆点表示本文的结果, 填充点为文献^[10]($\phi^* = 5.60$ 、 $n_{\text{ws}}^{1/3} = 1.46$ 、 $V^{2/3} = 4.38$ 、 $r = 2.45$ 、 $\mu = 0.04$) 的结果, 左右的点线表示 $\Delta H_{\text{exp}} \pm 30$ kJ/mol-atom 波动范围。可以看出, 在两端处模型计算值与实验值吻合较好, 但是在中间波动还是比较大, 主要为 Ti、Nb 的硫化物, 即

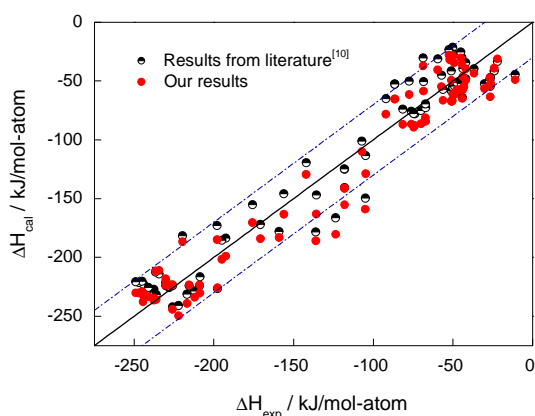


图2 过渡元素硫化物生成焓实验值与计算值之间的比较

Fig.2 Comparison between experimental and calculated enthalpies of formation of transition of oxides

TiS、TiS₂、TiS₃、Ti₂S₃、NbS、NbS₂、Nb₂S₃。由此部分元素的参数需要重新修正。表2给出了145个过渡元素、非过渡元素形成的硫化物体系生成焓的比较。

表2中就145个S的化合物生成焓进行了计算,就符号一致率而言,本文的结果中139个计算值符号与实验值^[10, 17-21]一致,符号一致率为95.9%,而文献^[10]中的结果为138个计算值符号与实验值一致,其一致率为95.17%。生成焓计算值与实验值符号不一致的有B₂S₃、P₄S₃、P₄S₅、P₄S₆、P₄S₇及P₄S₁₀,主要是B、P与S形成典型的共价化合物造成的,而Miedema模型对非过渡元素形成共价化合物生成焓的计算一直都不是太理想。本文的MAPE值为32.4%,文献^[10]中的MAPE值为30.1%,均比Sun的37.3%小很多。

表2 硫化物生成焓的结果比较

Table 2 Comparison of enthalpies of formation of sulfides (kJ/mol-atom)

Comp	ΔH_{exp}	ΔH_{cal}	$\Delta H_{\text{lit}}^{[10]}$	Comp	ΔH_{exp}	ΔH_{cal}	$\Delta H_{\text{lit}}^{[10]}$
LaS	-228.030	-223.613	-225.623	IrS _{2.667}	-45.004	-30.391	-25.352
La ₂ S ₃	-244.350	-237.854	-231.552	IrS ₃	-52.512	-28.090	-23.323
TiS	-135.981	-185.881	-178.313	Ir ₂ S ₃	-42.012	-39.747	-34.454
TiS ₂	-135.701	-163.1533	-146.881	NiS _{0.840}	-44.804	-57.282	-52.221
TiS ₃	-104.751	-128.902	-113.422	NiS	-43.935	-57.597	-51.612
Ti ₂ S ₃	-123.603	-180.455	-166.413	NiS ₂	-43.801	-46.436	-39.411
ZrS ₂	-192.464	-198.988	-183.623	Ni ₃ S ₂	-43.266	-54.724	-51.012
TaS ₂	-117.995	-141.454	-125.194	Ni ₃ S ₄	-43.042	-55.023	-48.023
CrS	-73.886	-87.913	-77.945	Ni _{0.958} S	-47.603	-57.451	-51.274
CrS _{1.170}	-76.161	-86.688	-75.702	Ni ₇ S ₆	-44.834	-57.392	-52.213
CrS _{1.2}	-70.012	-86.329	-75.211	PdS	-44.055	-64.981	-64.062
CrS _{1.330}	-67.092	-84.432	-72.882	PdS ₂	-30.273	-56.587	-52.431
Cr ₂ S ₃	-67.204	-81.410	-69.583	Pd ₃ S	-24.131	-39.157	-41.613
MoS ₂	-92.051	-78.280	-65.012	Pd ₁₆ S ₇	-26.802	-47.248	-49.723
MoS ₃	-77.402	-61.621	-50.093	Pd ₄ S	-22.083	-31.319	-33.432
Mo ₂ S ₃	-81.424	-86.959	-73.912	PtS	-41.954	-49.431	-48.161
WS ₂	-86.473	-65.340	-52.651	PtS ₂	-36.820	-43.503	-39.802
MnS	-107.101	-109.966	-101.182	CuS	-26.553	-63.528	-54.554
MnS ₂	-74.612	-89.471	-77.833	Cu ₂ S	-27.062	-54.238	-49.625
ReS ₂	-59.553	-40.590	-31.264	Ag ₂ S	-10.861	-48.996	-44.677
ReS ₃	-52.092	-31.937	-24.093	ThS	-197.703	-225.789	-226.55
Re ₂ S ₇	-50.161	-28.554	-21.452	ThS ₂	-208.674	-230.375	-216.587
Fe _{0.877} S	-56.192	-66.604	-57.201	Th ₂ S ₃	-216.803	-239.228	-231.366
Fe _{0.9} S	-50.463	-66.812	-57.522	US	-158.992	-183.131	-178.075
Fe _{0.920} S	-50.684	-66.961	-57.772	US ₂	-175.732	-170.438	-155.153

续表2

Comp	ΔH_{exp}	ΔH_{cal}	$\Delta H_{\text{lit}}^{[10]}$	Comp	ΔH_{exp}	ΔH_{cal}	$\Delta H_{\text{lit}}^{[10]}$
Fe _{0.940} S	-50.842	-67.080	-57.993	U ₂ S ₃	-170.803	-184.121	-172.082
Fe _{0.960} S	-50.641	-67.173	-58.193	PuS	-219.664	-186.726	-181.671
Fe _{0.980} S	-50.863	-67.239	-58.362	Pu ₂ S ₃	-197.903	-185.014	-172.994
FeS	-50.844	-67.282	-58.513	SrS	-234.303	-210.985	-214.153
FeS ₂	-57.181	-54.830	-45.092	BaS	-230.122	-218.100	-223.112
RuS ₂	-68.622	-37.259	-30.421	CaS	-236.601	-211.529	-212.552
OsS ₂	-49.233	-34.694	-27.462	PrS	-225.944	-244.154	-242.091
CoS _{0.890}	-50.034	-61.243	-54.992	Pr ₃ S ₄	-222.053	-249.773	-240.971
CoS	-49.002	-61.307	-54.421	NdS	-225.942	-223.330	-224.300
CoS ₂	-51.042	-49.469	-41.593	Nd ₂ S ₃	-237.601	-234.611	-227.102
Co ₃ S ₄	-68.373	-58.593	-50.663	Rh ₂ S ₃	-26.383	-52.541	-47.043
IrS ₂	-44.353	-35.719	-30.271	WS ₂	-86.393	-65.340	-52.654
Ge ₂ S ₃	-52.002	-32.249	-24.131	NbS ₂	-118.154	-141.094	-124.652
HgS	-26.672	-46.955	-39.224	NbS	-105.004	-158.961	-149.731
InS	-66.941	-62.771	-54.903	Nb ₂ S ₃	-118.003	-155.364	-140.662
In ₂ S ₃	-71.133	-64.215	-54.051	SmS	-215.483	-223.494	-224.133
In ₂ S ₆	-70.372	-64.481	-55.462	YS	-230.003	-223.309	-223.872
InS _{1.33}	-72.103	-64.691	-55.093	VS	-142.124	-129.545	-119.553
P ₄ S ₃	-32.031	4.771	8.614	CeS	-228.003	-223.641	-225.182
P ₄ S ₅	-33.885	4.999	8.595	Ce ₂ S ₃	-237.652	-236.535	-229.673
P ₄ S ₆	-34.723	5.000	8.5922	CeS _{1.333}	-236.122	-235.838	-231.604
P ₄ S ₇	-29.395	4.590	7.661	DyS	-230.002	-222.817	-222.816
P ₄ S ₁₀	-22.094	3.838	6.262	Dy ₂ S ₃	-244.001	-231.454	-222.893
Sb ₂ S ₃	-28.352	-38.733	-29.953	ErS	-230.003	-222.712	-222.332
SiS ₂	-71.131	-23.702	-16.014	Er ₂ S ₃	-247.004	-230.369	-221.421
SnS	-53.971	-52.468	-44.832	EuS	-209.005	-223.433	-224.042
SnS ₂	-51.182	-51.117	-40.931	EuS _{1.333}	-212.024	-233.861	-228.534
Sn ₂ S ₃	-52.723	-54.212	-44.602	GdS	-230.003	-223.309	-223.875
Sn ₃ S ₄	-52.904	-54.445	-45.303	Gd ₂ S ₃	-241.002	-233.474	-225.512
Tl ₂ S	-31.663	-39.799	-35.414	HfS ₂	-195.001	-201.736	-185.451
ZnS	-95.922	-57.093	-48.492	HfS ₃	-156.003	-163.354	-146.022
Na ₂ S	-122.031	-78.327	-76.674	HoS	-230.004	-220.921	-220.703
Na ₂ S ₂	-98.324	-107.633	-101.457	Ho ₂ S ₃	-245.002	-229.097	-220.384
Na ₂ S ₃	-86.533	-109.608	-99.568	LuS	-230.001	-223.733	-222.932
Na ₂ S ₄	-68.552	-101.1412	-89.563	Lu ₂ S ₃	-249.005	-230.149	-220.721
K ₂ S ₂	-107.752	-109.043	-105.312	AsS	-14.054	-24.198	-17.392
K ₂ S ₃	-93.564	-120.019	-112.573	As ₂ S ₃	-16.603	-24.234	-16.743
K ₂ S	-125.523	-75.100	-73.761	AlS	-132.002	-57.115	-48.274
K ₂ S ₄	-77.622	-118.078	-107.903	Al ₂ S ₃	-144.801	-54.740	-44.522

续表 2

Comp	ΔH_{exp}	ΔH_{cal}	$\Delta H_{\text{lit}}^{[10]}$	Comp	ΔH_{exp}	ΔH_{cal}	$\Delta H_{\text{lit}}^{[10]}$
K ₂ S ₅	-70.86	-110.518	-99.005	B ₂ S ₃	-50.463	7.553	12.401
K ₂ S ₆	-58.533	-101.255	-89.402	Bi ₂ S ₃	-28.624	-44.812	-35.282
BeS	-117.152	-4.354	2.301	CdS	-74.683	-57.632	-49.593
MgS	-172.864	-103.605	-95.803	EuS	-209.202	-149.488	-145.002
PbS	-49.323	-44.049	-36.234	GaS	-104.601	-60.910	-52.562
SiS ₂	-78.331	-23.702	-16.011	Ga ₂ S ₃	-103.262	-59.830	-49.661
Rb ₂ S	-121.333	-74.446	-73.254	GeS ₂	-52.304	-29.147	-21.292
Cs ₂ S	-114.003	-73.184	-72.101	GeS	-38.001	-33.246	-25.873
Li ₂ S	-223.004	-98.996	-98.045				

3 相互作用系数的计算

鉴于本文的最初动机, 提供高温熔体中 O 和 S 的热力学数据。以下将结合 Ding 提出的三元合金高温熔体活度相互作用系数的计算公式, 给出 1873 K 下 Fe 基熔体中 O 和 S 与其他元素之间的相互作用系数。Ding 给出的计算公式^[6, 7]为

$$\varepsilon_i^j = \frac{1}{RT} \left\{ f_{ij} [1 + \mu_i(\phi_i^* - \phi_j^*)] / V_j^{2/3} - f_{ik} [1 + \mu_i(\phi_i^* - \phi_k^*)] / V_k^{2/3} - f_{jk} [1 + \mu_j(\phi_j^* - \phi_k^*)] / V_k^{2/3} \right\} \quad (3)$$

其中

$$f_{ij} = \frac{2pV_i^{2/3}V_j^{2/3}}{(n_{\text{ws}}^{1/3})_i^{-1} + (n_{\text{ws}}^{1/3})_j^{-1}} \times \left[\frac{q}{p} (\Delta n_{\text{ws}}^{1/3})_{ij}^2 - (\Delta \phi^*)_{ij}^2 - a \left(\frac{r}{p} \right) \right]$$

$$f_{ik} = \frac{2pV_i^{2/3}V_k^{2/3}}{(n_{\text{ws}}^{1/3})_i^{-1} + (n_{\text{ws}}^{1/3})_k^{-1}} \times \left[\frac{q}{p} (\Delta n_{\text{ws}}^{1/3})_{ik}^2 - (\Delta \phi^*)_{ik}^2 - a \left(\frac{r}{p} \right) \right]$$

$$f_{jk} = \frac{2pV_j^{2/3}V_k^{2/3}}{(n_{\text{ws}}^{1/3})_j^{-1} + (n_{\text{ws}}^{1/3})_k^{-1}} \times \left[\frac{q}{p} (\Delta n_{\text{ws}}^{1/3})_{jk}^2 - (\Delta \phi^*)_{jk}^2 - a \left(\frac{r}{p} \right) \right]$$

将本文的结果代入上式, 计算 O 与其它元素之间相互作用系数, 如表 3 所示。

表 3 给出了本研究 O 与其它相互作用系数计算值与对应实验值的比较。图 3-图 6 分别给出了每个周期元素的计算结果与实验值的比较, 图 3 为 O 与主族元素之间相互作用系数的结果比较, 图 4-图 6 为过渡元素周期的结果比较。可以看出, 计算值与实验值曲线整体的变化趋势是比较一致的。其中过渡元素其计算结果与实验值比较接近, 如 $\varepsilon_0^{\text{Mn}}$ 计算值 -6.90, 实验值 -4.73; 而对主族元素, 计算值与实验值之间的误差比较大, 如 ε_0^{P} , ε_0^{C} 计算值分别为 21.91, 34.90, 对应的实验值却为 -13.20, -19.96。从

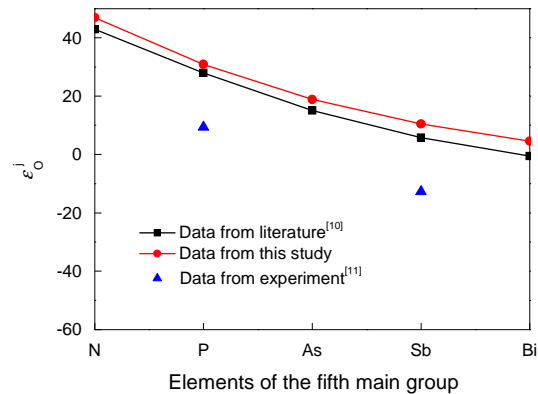


图 3 Fe 基溶液 1873 K 时第五主族元素与对应的 ε_0^j 实验值与计算值之间的关系

Fig.3 Relation between experimental and calculated ε_0^j of the fifth main group elements in liquid Fe at 1873 K

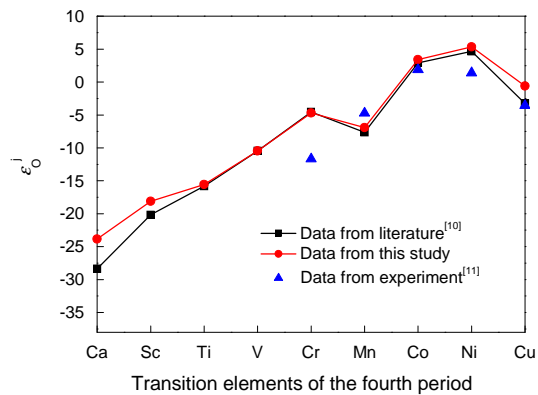


图 4 Fe 基溶液 1873 K 时第四周期元素与对应的 ε_0^j 实验值与计算值之间的关系

Fig.4 Relation between experimental and calculated ε_0^j of the fourth periodic elements in liquid Fe at 1873 K

图 3-图 6 也可以看出, j 越接近 Fe, 即其性质与 Fe 越相似时, 计算值与实验值之间的差值越小。

表 4 给出了硫与其它元素之间相互作用系数计算值与实验值之间的比较。由表 4 及图 7-10 可以看

表3 ϵ_0^j 实验值与计算值的比较
Table 3 Comparison between experimental and calculated ϵ_0^j

Element	Lit ^[10]	Cal	Exp ^[11]	Element	Lit ^[10]	Cal	Exp ^[11]
Ca	-28.38	-23.85		Be	12.02	14.13	
Sc	-20.16	-18.11		B	20.13	21.91	-13.20
Ti	-15.82	-15.55		C	32.21	34.90	-19.96
V	-10.44	-10.48		N	42.90	46.91	-7.30
Cr	-4.56	-4.70	-11.68	Na	-20.10	-14.67	
Mn	-7.63	-6.90	-4.73	Mg	-9.61	-5.72	
Co	2.92	3.44	1.89	Al	5.49	8.71	
Ni	4.66	5.36	1.40	Si	13.04	16.09	-7.09
Cu	-3.26	-0.58	-3.56	P	27.94	30.88	9.36
Sr	-31.73	-26.84		K	-28.47	-22.69	
Y	-21.50	-18.88		Zn	1.71	5.39	
Zr	-17.67	-16.54		Ga	3.44	7.21	
Nb	-12.50	-13.01		Ge	9.67	13.61	
Mo	-4.55	-5.12	1.26	As	15.13	18.85	
Tc	6.58	6.85		Rb	-30.84	-25.04	
Ru	8.42	8.67		Cd	-0.59	3.70	
Rh	8.45	9.38	5.08	In	-1.92	2.73	
Pd	9.12	11.02	-4.81	Sn	2.54	6.99	-6.50
Ag	-5.84	-2.12	-5.81	Sb	5.80	10.45	-12.70
Ba	-33.63	-28.68		Cs	-33.09	-27.28	
La	-22.65	-19.75		Hg	0.12	4.64	
Hf	-17.32	-16.72		Tl	-4.14	0.91	
Ta	-12.52	-12.92		Pb	-1.95	3.16	
W	-2.27	-2.95	4.52	Bi	-0.56	4.54	
Re	4.58	4.28		Dy	-21.19	-18.66	
Os	8.40	8.45		Ho	-21.20	-18.65	
Ir	11.46	11.94		Er	-20.90	-18.45	
Pt	13.67	14.79	1.52	Tm	-20.91	-18.47	
Au	7.32	10.20	-8.18	Yb	-20.92	-18.48	
Nd	-21.84	-19.13		Lu	-20.64	-18.31	
Pm	-21.47	-18.87		Th	-18.99	-16.94	
Sm	-21.50	-18.87		U	-14.38	-13.76	
Eu	-21.50	-18.87		Pu	-16.24	-15.04	
Gd	-21.50	-18.88		Ce	-22.23	-19.42	
Tb	-21.18	-18.64		Pr	-21.85	-19.13	
Li	-14.48	-10.01		H	18.97	22.72	3.98

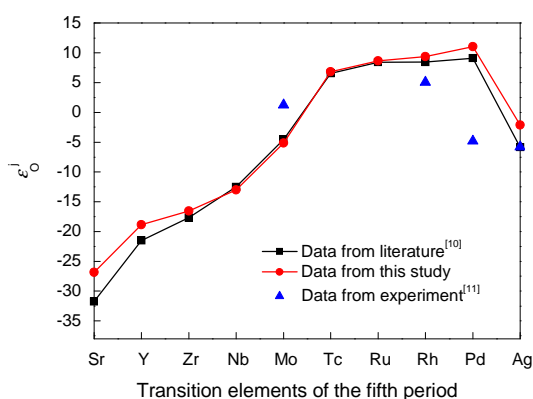


图5 Fe基溶液 1873 K 时第五周期元素与对应的 ε_0^j 实验值与计算值之间的关系

Fig.5 Relation between experimental and calculated ε_0^j of the fifth periodic elements in liquid Fe at 1873 K

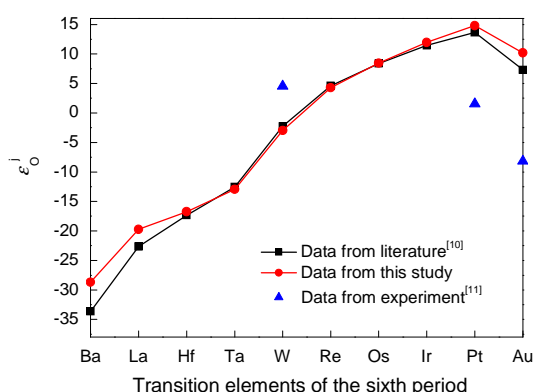


图6 Fe基溶液 1873 K 时第六周期元素与对应的 ε_0^j 实验值与计算值之间的关系

Fig.6 Relation between experimental and calculated ε_0^j of the sixth periodic elements in liquid Fe at 1873 K

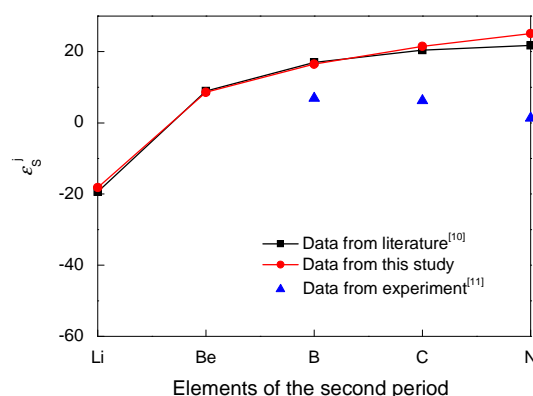


图7 Fe基溶液 1873 K 时第二周期元素与对应的 ε_s^j 实验值与计算值之间的关系

Fig.7 Relation between experimental and calculated ε_s^j of the second periodic elements in liquid Fe at 1873 K

出,在总体上实验值与计算值之间的误差不大。图7为主族元素计算的结果,可见主族元素对应的计算值与实验值之间的误差较大。图8-10为过渡族

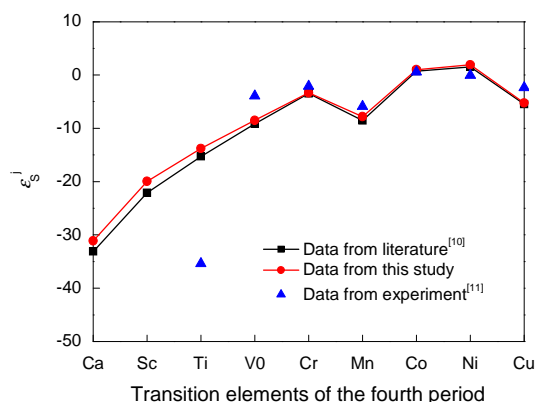


图8 Fe基溶液 1873 K 时第四周期元素与对应的 ε_s^j 实验值与计算值之间的关系

Fig.8 Relation between experimental and calculated ε_s^j of the fourth periodic elements in liquid Fe at 1873 K

元素计算的结果比较,与图7相比,过渡族元素的计算结果精度有了很大的提高,如 $\varepsilon_s^{\text{Mn}}$, $\varepsilon_s^{\text{Cr}}$ 计算值分别为-8.54、-3.44,而其对应的实验值则为-5.86、-2.13。由图7-10可以看出,当 j 元素越接近Fe时, ε_s^j 计算值与实验值就越接近,且相互作用系数计算值与实验值基本都符合元素周期性规律。

4 Nb、Ag、Pt 参数的修正

在研究过程中,误差较大的化合物主要有碱土元素的过氧化物(CaO_2 、 BaO_2 、 SrO_2),贵金属元素的氧化物(Rh_2O_3 、 RhO 、 Rh_2O 、 Pt_2O_3 、 Ag_2O 、 Au_2O_3 、 PdO)及 CuO 、 Cu_2O 、 NbS 、 NbS_2 、 Nb_2O_3 、 Ti_2S_3 、 TiS_3 、 TiS 、 TiS_2 。本文对初步选定的Ag、Pt、Nb的参数进行重新给定,从而提高Miedema模型计算的精度。完成对元素参数重新给定的前提是有可靠的实验数据,自上世纪80年代以来,Kleppa等采用量热测定法给出了362个化合物的生成焓,使本文的研究有了一定的可能性。为了保证实验数据的精度,同一化合物生成焓不同实验者得出的结果相差不大于 ± 10 kJ/mol-atom,如 TbPt_3 见报道的实验值有-85.6 kJ/mol-atom和-63.9 kJ/mol-atom,在此将不予考虑。而通过Miedema模型的研究可以发现,对计算结果起决定作用的还是电负性 ϕ_{exp}^* ,因此以下将二元合金生成焓的实验值与Miedema模型相结合,在改变电负性 ϕ_{exp}^* 的同时不断优化电子密度 n_{ws} ,摩尔体积 V 。对以同一元素为基的一系列化合物得出相应的 ϕ_{exp}^* 值后,求其平均数。

4.1 Nb 电负性参数的修正

通过Nb的二元化合物生成焓实验值与Miedema计算模型相结合,得出电负性的平均值为 $\phi_{\text{revised}}^* = 4.31$,相对原始的4.05有了很大的改动。而

表4 ε_s^j 实验值与计算值得比较
Table 4 Comparison between experimental and calculated ε_s^j

Element	Lit ^[10]	Cal	Exp ^[11]	Element	Lit ^[10]	Cal	Exp ^[11]
Ca	-31.12	-33.12		Au	2.21	1.88	-0.25
Sc	-19.95	-22.07		Nd	-22.64	-24.75	
Ti	-13.78	-15.27		Pm	-22.09	-24.22	
V	-8.49	-9.15	-3.89	Sm	-22.16	-24.27	
Cr	-3.33	-3.44	-2.13	Eu	-22.16	-24.27	
Mn	-7.79	-8.54	-5.86	Gd	-22.16	-24.27	
Co	1.01	0.71	0.58	Tb	-21.70	-23.82	
Ni	1.91	1.49	-0.054	Dy	-21.72	-23.83	
Cu	-5.23	-5.49	-2.35	Ho	-21.77	-23.86	
Sr	-35.07	-37.04		Er	-21.29	-23.40	
Y	-22.16	-24.27		Tm	-21.30	-23.42	
Zr	-17.03	-18.94		Yb	-21.31	-23.43	
Nb	-9.18	-9.97	-5.63	Lu	-20.85	-22.99	
Mo	-2.29	-2.13	0.35	Th	-18.81	-20.85	
Tc	4.43	4.32		U	-13.17	-14.57	
Ru	5.89	5.78		Pu	-15.95	-17.69	
Rh	4.22	3.59		Ce	-23.16	-25.26	
Pd	2.45	1.22		Pr	-22.64	-24.75	
Ag	-8.97	-9.20		H	11.49	11.16	2.67
Ba	-37.35	-39.43		Li	-18.21	-19.38	
La	-23.71	-25.80		Be	8.56	8.96	
Hf	-15.70	-17.61		B	16.45	17.01	6.86
Ta	-9.45	-10.29	-10.34	C	21.48	20.39	6.26
W	-0.17	0.23	6.03	N	25.05	21.70	1.32
Re	4.35	4.70		Na	-25.32	-26.02	
Os	6.37	6.43		Mg	-12.76	-13.50	
Ir	7.57	7.20		Al	2.25	2.04	5.06
Pt	7.68	6.75	4.65	Si	8.76	8.76	9.12
In	-6.91	-7.17		P	20.50	20.20	4.90
Sn	-2.67	-2.88	-3.27	K	-34.71	-35.41	
Sb	-0.40	-0.56	0.67	Zn	-2.12	-2.39	
Cs	-40.06	-40.82		Ga	-0.54	-0.81	
Hg	-5.34	-5.53		Ge	4.20	4.03	3.89
Tl	-9.76	-9.91		As	9.26	9.11	0.92
Pb	-8.08	-8.17	-41.80	Rb	-37.42	-38.16	
Bi	-6.79	-6.89		Cd	-5.33	-5.59	

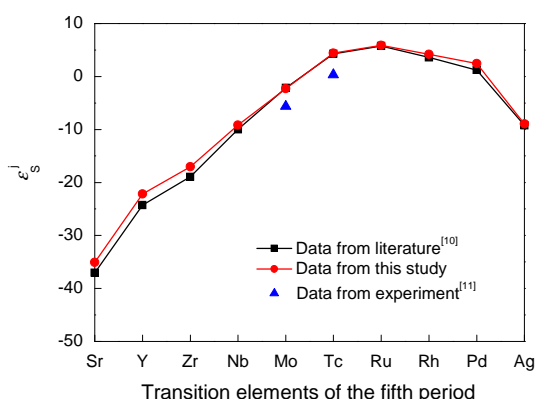


图 9 Fe 基溶液 1873 K 时第五周期元素与对应的 ε_s^j 实验值与计算值之间的关系

Fig.9 Relation between experimental and calculated ε_s^j of the fifth periodic elements in liquid Fe at 1873 K

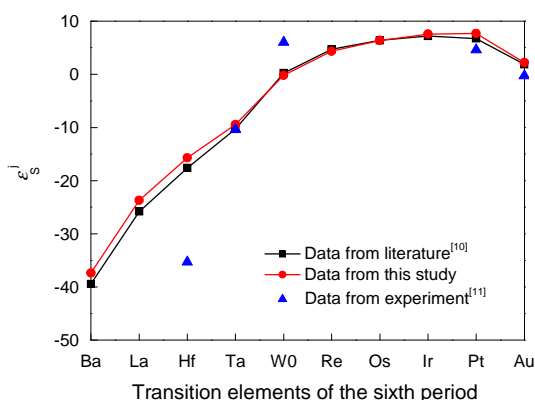


图 10 Fe 基溶液 1873 K 时第六周期元素与对应的 ε_s^j 实验值与计算值之间的关系

Fig.10 Relation between experimental and calculated ε_s^j of the sixth periodic elements in liquid Fe at 1873 K

计算的结果也表明, 改动前后的数据对结果有着很大的影响。

图 11 给出了 Nb 基二元化合物生成焓实验值与原始计算值、改进参数后计算值之间的比较。通过对比可以看出, 改进后的计算数据明显向实验值靠近, 如 Nb₆Fe, 生成焓采用原参数的计算值为 $\Delta H_{\text{original}} = -23.37 \text{ kJ/mol-atom}$, 而当 $\phi_{\text{Nb}} = 4.31$ 时 $\Delta H_{\text{revised}} = -8.52$, 与实验值 -6.2 kJ/mol-atom 更加的接近。把 Nb 的参数代入 Nb-S 合金体系计算, 以验证所得参数的可行性。NbS₂, NbS, Nb₂S₃ 三者生成焓对应的实验值分别为 $-118.15 \text{ kJ/mol-atom}$, $-105.00 \text{ kJ/mol-atom}$, $-118.00 \text{ kJ/mol-atom}$, 改进 Nb 参数后的计算值分别为 -119 kJ/mol-atom , -133 kJ/mol-atom , -131 kJ/mol-atom , 而 Miedema 原数据的计算值为 $-141.09 \text{ kJ/mol-atom}$, $-158.96 \text{ kJ/mol-atom}$, $-155.34 \text{ kJ/mol-atom}$ 。由此可见, 改进后的参数更适

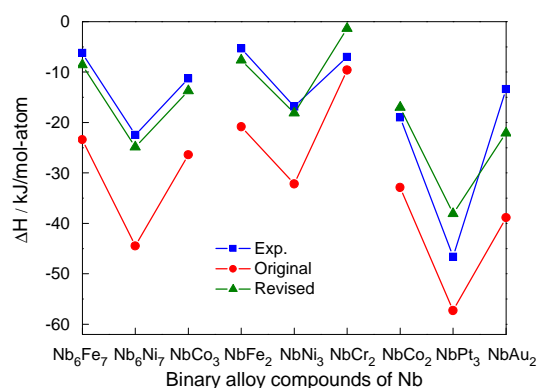


图 11 Nb 基二元合金生成焓实验值^[22-28]与计算值之间的比较

Fig.11 Comparison between calculated and experimental enthalpies of formation of Nb-compounds

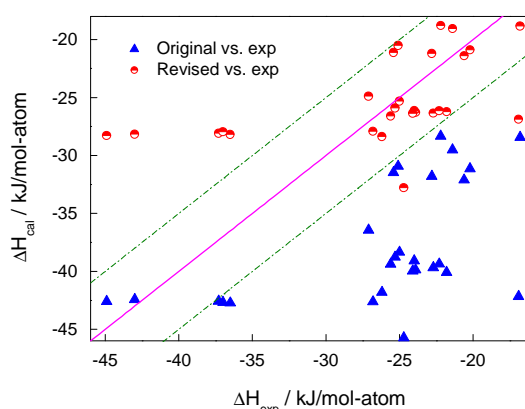


图 12 Ag 基化合物实验值与计算值之间的比较

Fig.12 Comparison between calculated and experimental enthalpies of formation of Ag-compounds

合于 Miedema 模型的计算。

4.2 Ag 电负性参数的修正

通过 Miedema 模型与实验数据相结合, 本文将 Ag 的电负性值由 4.35 改为 4.17, 其二元合金化合物生成焓实验值^[29-31]与计算值之间的比较如图 12 所示。

图 12 给出了镧系元素与 Ag 形成 27 个二元合金化合物生成焓实验值与原始计算值、改进参数后计算值之间的比较。图中实线表示计算值与实验值 100% 相等; 点线表示 $\Delta H_{\text{exp}} \pm 5 \text{ kJ/mol-atom}$ 。当 Ag 的电负性 ϕ_{Ag} 由 4.35 变为 4.17 之后, 其生成焓实验值与计算值之间的误差有了很大的改进。使用原始数据计算的生成焓数值只有 2 个点落在波动范围之内 ($\Delta H_{\text{exp}} \pm 5 \text{ kJ/mol-atom}$)。 $\phi_{\text{Ag}} = 4.17$ 时的计算结果有了明显的好转, 27 个点中有 20 个落在波动范围之内。同时图 12 中还有个别的点, 改进参数后计算值与实验值还存在较大的误差, 主要有 AgEr、

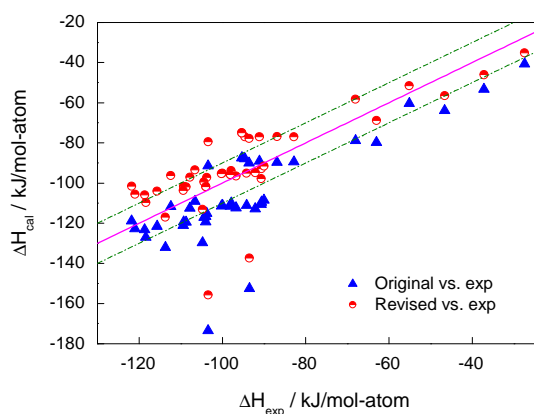


图 13 Pt 基化合物生成焓实验值与计算值的对比

Fig.13 Comparison between experimental and calculated data of enthalpies of formation of Pt-compounds

AgTm、AgDy、AgSm、AgTb、Ag₂Pr、AgLa。并不是改进后的参数不适于这些化合物组成元素的体系,如 Ag-Er 之间形成的化合物。虽然 AgEr 生成焓实验值(-44.90 kJ/mol-atom)与计算值(-28.28 kJ/mol-atom)之间的误差较大,但是 Ag₂Er、Ag₃Er 生成焓的实验值(-24.00 kJ/mol-atom, -25.40 kJ/mol-atom)与计算值(-26.12 kJ/mol-atom, -21.11 kJ/mol-atom)却吻合得很好,这是 Miedema 模型精度的问题。该模型只是个半经验模型,因此模型计算值并不能与实验值完全一致。

4.3 Pt 电负性的修正

图 13 给出了 Pt 的电负性由 5.65 改为 5.57 后生成焓实验值与 Miedema 模型原始计算值、改进参数 Miedema 模型计算值之间的对比。图中实线表示计算值与实验值相等;点线表示 $\Delta H_{\text{exp}} \pm 10$ kJ/mol-atom。由于电负性值变化不大,改进前后计算数值的变化不大,因为改进后的数值对称性更好。参数改变前的计算数值有 16 个在波动范围($\Delta H_{\text{exp}} \pm 10$ kJ/mol-atom)之内,而 $\phi_{\text{Pt}}=5.57$ 计算的结果 44 个数值中有 28 个落在波动范围之内。

5 结 论

1. 将过渡元素氧化物生成焓的实验数据与 Miedema 模型相结合,得到了 O 的参数:电负性 7.04,摩尔体积 4.59,边界电子密度 6.03, $r=2.5$, $\mu=0.04$ 。把所得参数应用于 141 种过渡元素、非过渡元素氧化物体系,得到 Miedema 模型生成焓的计算值与实验值之间 MAPE 值为 36.8%, 100% 的符号一致。将所得结果代入 Ding 提供的相互作用系数计算公式,给出了 1873 K 时 Fe 基熔体中 O 与其它元素之间相互作用系数,计算值与实验值之间误差不大且变化趋势比较一致。

2. 用相同方法可得到 S 适于 Miedema 模型的参数:电负性 5.80,摩尔体积 6.97,电子密度 3.24, $r=2.5$, $\mu=0.04$ 。通过对 145 个过渡元素,非过渡元素硫化物生成焓实验值与计算值的对比,得出 MAPE 值为 32.4%,符号一致率为 95.9%。对 S 与其它元素相互作用系数的计算结果表明,在总体上计算值与实验值之间的误差不大。

3. 将实验数据与 Miedema 模型相结合,并将 Nb、Ag、Pt 的电负性由 4.05、4.35、5.65 修正为 4.31、4.17、5.57,计算值与实验值更接近。

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