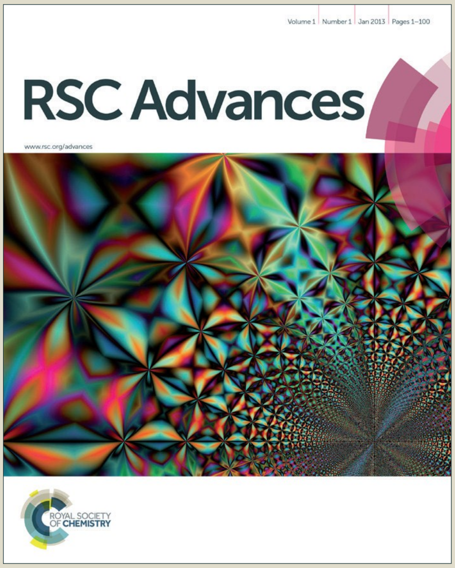
RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

# Reactive wetting of Ni-Si alloys on graphite substrate: Effects of Si and Ni

Tingting Wang, Yuan Yang, Yong Bin Ren, Dingyi Zhu* and Teng Zhang*
College of Materials Science and Engineering, Fuzhou University, Fuzhou, Fujian 350108, China

In recent years, the reactive wetting of Ni-Si on graphite attracts increasing attentions. However, most attentions have been focused on the effect of Si on the wetting behavior of Ni-Si/C systems. In this work, the wetting process of Ni-Si alloys with different Si contents (20, 28, 35, 45 and 55 wt%) on graphite substrate has been investigated at 1523 K in high vacuum using a modified sessile drop method. The threshold activity of Si in liquid to form SiC at 1523 K can be calculated to be 0.0173, corresponding for a Si content of 33 at% (19 wt%). In addition, a minimum equilibrium contact angle of 20° can be observed in the Ni-45 wt% Si/C system. The adsorption energy of Si at the interface and at the surface of metal Ni are 5.36 kJ/mol and -20.9 kJ/mol, respectively; whereas, the adsorption energy of Ni at the interface and at the surface of metal Si are -5.38 kJ/mol and 68.9 kJ/mol, respectively. Moreover, the effects of Si and Ni on the change of equilibrium contact angle have been evaluated in terms of the solid-liquid interfacial energy and the surface energy of liquid alloy.

**Key Words:** Reactive wetting; Threshold activity; Adsorption energy; Solid-liquid interfacial energy; Surface energy

---

* Corresponding author. Tel.: +86 0591 22866540; fax.: +86 0591 22866537; E-mail address: zdy7081@163.com.
* Corresponding author. Tel.: +86 591 22866540; fax.: +86 591 22866537. E-mail address: teng_zhang@fzu.edu.cn (T. Zhang).

RSC Advances Accepted Manuscript

RSC Advances Accepted Manuscript

# 1. Introduction

The field of wetting surface attracts increasing attention in recent years.[1-6] In particular, the wetting behavior of metal matrix composites on the ceramic substrates, such as the Me-Si/graphite system (Me = Cu, Al, Fe), [7-11] is of great interest, which includes the reaction infiltration of liquids Si into graphite, and results in the formation of "reaction bond carbide" or SiC composites.[12, 13] It is well established that the surface active elements Si plays an important role on the reactive wetting process in Ni-Si/C system. Si can react with graphite to form the wettable SiC, which leads to the decrease in solid-liquid interfacial energy, and thus promotes the spreading of liquid alloy.[14-18] In addition, Si can reduce the surface energy of liquid alloy (i.e., Ni, Cu, Au, Fe).[19-21]

On the other hand, Ni is also critical for the wetting behavior of many alloys. U.Gangopadhyay et al.[22] reported that the equilibrium contact angle of Au/C can be decreased by 7.8 ° with the addition of 15 at% Ni, due to the adsorbed Ni layer at the interface. This was also verified by the crater-edge profiling experiment. In addition, P.Wynblatt et al. found that the contact angles of Pb/C system decreased with increasing Ni content. The adsorption content of Ni at the interface, measured by CEP technique, also increased with increasing Ni content.[23] However, most attentions have been focused on the effect of Si on the reactive wetting of Ni-Si/C systems. In this work, the wetting process of three Ni-Si alloys, with different Si contents (20, 28, 35, 45 and 55 wt%), on porous graphite substrate has been investigated at 1523 K in high vacuum, using a modified sessile drop method. Particular attention has been focused on the effects of Si and Ni on the wetting process of Ni-Si/C to provide comprehensive information on the fundamentals of this important wetting system.

## 2. Experimental procedure

The high purity graphite plates (99.99 wt%, Toyo Carbon, Japan) with a density of 1.82 g/cm$^3$ were used as substrates with an ash content less than 20 ppm. Before the wetting experiments, the surfaces of substrates were mechanically polished by diamond paste to obtain an average roughness of 19 nm. The Ni-Si alloys with Si contents, 20, 28, 35, 45 and 55 wt% in nominal compositions, were prepared by arc-melting of high-purity Ni (99.999 wt%, Alfa Aesar China, Tianjin, China) and Si (99.999 wt%, Alfa Aesar China, Tianjin, China) plates in argon (99.999% purity). The specimens were referred to as Ni-20 wt% Si, Ni-28 wt% Si, Ni-35 wt% Si, Ni-45 wt% Si and Ni-55 wt% Si, respectively. The raw materials were melted and solidified in a water-cooled copper crucible for four times with the assistance of electromagnetism stirring to ensure the chemical homogeneity of resulting alloys. Then the alloys were cut into cubes for wetting experiments. Both the graphite plates and Ni-Si cubes were ultrasonically cleaned in alcohol.

The wetting behaviors of Ni-Si alloys were investigated by a modified sessile drop method in an average vacuum of 10$^{-4}$ pa. Detailed description of the experiment procedure was given elsewhere.[24, 25] In brief, the alloys and substrates were separated before the experiment to avoid the pre-interaction upon heating. Once reaching the desired temperature, the alloy was dropped on the graphite substrate through an $Al_2O_3$ tube. The wetting process was recorded by a charge-coupled device camera (1504×1000 pixels), as shown in Fig.1

Some wetting couples were cross-sectioned by a diamond saw and polished for microstructure observation using scanning electron microscopy (Supra-55, Zeiss, Jena, Germany) coupled with energy-dispersive X-ray spectroscopy (X-Max, OXFORD instruments, Oxford, England) analysis.

RSC Advances Accepted Manuscript

RSC Advances Accepted Manuscript

## 3. Results and discussion

Fig.2 shows the cross-section of Ni-Si/C systems after held at 1523 K in vacuum for 90 min. It is clear that a continuous layer of SiC (~ 3um) can be observed at the interface between the alloy and graphite substrate (in Fig.2a-2c). In addition, some faceted SiC crystals present above the reaction layer in the Ni-45wt%Si/C system (in Fig.2d). Similar results have also been reported in Ni-Si/C systems[15, 16]and Cu-Si/C systems.[16] Moreover, the morphology of $NiSi_2$ phase (dark regions) changes from dendrites (in Fig.2a) to spheres (in Fig.2c) when the Si content increases from 35 to 55 wt%. B.A. Julies also reported that great content of Si promotes the growth of $NiSi_2$ phase in Ni-Si alloys due to the reaction between excess Si and matrix.[26]

The activity of a compound in a given system can be formed as:

$$a_z = \exp[(u_z - u_\theta^z)/RT] \tag{1}$$

Where $u_z$ is the chemical potential of Z component, $\mu_Z^\theta$ is the mole Gibbs energy of pure Z and R is gas constant. Fig.3 shows the activity of Si and Ni in Ni-Si binary alloys at 1523 K. It is clear that the activity of Si and Ni increases significantly at the Si/Ni fraction (in molar) of about 0.3 and 0.6, respectively.

By assuming that the formation of SiC only depends on the Si content rather than C, the threshold activity of Si in liquid to form SiC, $a_{si}(SiC)$ can be calculated using following equations:[14, 25, 28]

$$a_{si}(SiC) = \frac{1}{a_c^{Ni}} \exp\left[\frac{\Delta G_f^0(SiC)}{RT}\right] \tag{2}$$

$$\Delta G_f^0(T) = -113482 + 37.4872T \tag{3}$$

Where $a_c^{Ni}$ is the activity of C in liquid Ni-C with supersaturated dissolution of graphite, $\Delta G_f^0(T)$ is the Gibbs energy of formation of SiC from pure molten Si and solid C. The threshold activity of Si in liquid to form SiC at 1523 K can be calculated to be 0.0173. Correspondingly, the threshold content of Si in liquid Ni-Si alloy at 1523 K is about 33 at% (19 wt%), in good agreement with previous works in literature.[15]

Fig.4 shows the change of contact angles in Ni-Si/C system at 1523 K as a function of time. It is clear that the contact angle of all specimen decreases with increasing time. In addition, a minimum equilibrium contact angle of 20° can be observed in the Ni-45 wt% Si/C system. Similar results have been found in other alloy systems, including Au-Si/SiC,[29, 30] Cu-Ti/SiC,[31] Ag-Zr/AlN,[32] and Sn-Al/$Al_2O_3$, which could be attributed to the change in energy of adsorption by varying compositions.[33] It is also known that the equilibrium contact angle in a reactive wetting system corresponds to the contact angle of the alloy on the reaction product.[15, 16] The equilibrium contact angle in present work can thus be associated with the contact angle of Ni-Si on SiC.

To explain the change of equilibrium contact angle by components in this work, the chemical adsorption of Ni and Si on SiC has been evaluated by the Gibbs adsorption equation[34] as followed:

$$d\sigma = -\Gamma_{A/B} du_A \tag{4}$$

Where $\sigma$ is the solid-liquid interfacial energy, $\Gamma_{A/B}$ is the relative adsorption of element A with respect to element B, $\mu_A$ is the chemical potential of component A. As for the Ni-Si/C system, the equation (4) can be written as followed:

$$\left\{ \begin{array}{l} \Gamma_{Ni/Si} = -\dfrac{d\sigma_{SL}}{RTd\ln(a_{Ni})} \\ \Gamma_{Si/Ni} = -\dfrac{d\sigma_{SL}}{RTd\ln(a_{Si})} \end{array} \right\} \tag{5}$$

RSC Advances Accepted Manuscript

Where $a_{Ni}$ is the activity of Ni in liquid alloy and $a_{Si}$ is the activity of Si in alloy. In addition, the relative adsorption of Ni with respect to Si can be calculated by following equation:[34, 35]

$$\Gamma_{Ni/Si}\Omega_M = 1 - \frac{y_{Si}}{x_{Si}} \tag{6}$$

Where $\Omega_M$ is the molar interfacial area of the liquid alloy (40500 $m^2$/mol for Ni-Si system[36]), $y_{Ni}$ is the molar fraction of Ni at the last layer of liquid contacted with SiC, $x_{Ni}$ is the molar fraction of Ni in bulk liquid. Furthermore, the work of immersion $W_i$ can be calculated as followed:

$$W_i = \sigma_{SL} - \sigma_{SV} = -\sigma_{LV} \cdot \cos\theta \tag{7}$$

Where $\sigma_{SL}$ is the solid-liquid interfacial energy, $\sigma_{SV}$ is the surface energy of the solid, $\sigma_{LV}$ is the surface energy of liquid alloy,[15, 19] $\theta$ is the equilibrium contact angle.

Based on the equation (7), the value of ($\sigma_{SL} - \sigma_{SV}$) can be associated with the activity of Si or Ni in liquids ($a_{Si}$ or $a_{Ni}$), as shown in Fig.5. Based on the slopes of Fig.5, the relative adsorption of Ni and Si at the interface, $\Gamma_{Ni/Si}$ and $\Gamma_{Si/Ni}$ can be calculated to be $8.51\times10^{-6}$ and $-1.26\times10^{-5}$, respectively. Based on the equation (6), $y_{Si}/x_{Si}$ and $y_{Ni}/x_{Ni}$ can be calculated to be 0.655 and 1.53, respectively. C. Rado et al. reported that $y_{Ni}/x_{Ni}$ ranges from 1.43 to 1.91 when the Ni content in NiSi system increases from 15 to 60 (in mole%).[34] This further confirms the adsorption of Ni on SiC in present work.

On the other hand, the adsorption energy of Si at the interface ($E_{SL}(Si)_{Ni}$) and at the surface of metal Ni ($E_{LV}(Si)_{Ni}$) can be described by following equations.[33-35]

RSC Advances Accepted Manuscript

$$\left(\frac{y_{Si}}{x_{Si}}\right)_{x_{si\to 0}} = \exp\left[\frac{-E_{SL}(Si)_{Ni}}{RT}\right] \tag{8}$$

$$E_{LV}(Si)_{Ni} = (\sigma_{LV}^{Si} - \sigma_{LV}^{Ni})\Omega - m\lambda \tag{9}$$

Where $\sigma_{LV}^{Si}$ and $\sigma_{LV}^{Ni}$ are the surface energy of pure Ni and Si ( $\sigma_{LV}^{Ni} = 1.83 \pm 0.09$ J/m$^2$, $\sigma_{LV}^{Si} = 0.72 \pm 0.04$ J/m$^2$),[19, 34] $\lambda$ is the exchange energy of the alloy (-96 kJ/mol)[34, 37] and $m$ is a structural parameter (0.25). [34] Based on the equations (8) and (9), one can calculate that $E_{SL}(Si)_{Ni}$ and $E_{LV}(Si)_{Ni}$ are 5.36 kJ/mol and -20.9 kJ/mol, respectively. Similarly, $E_{SL}(Ni)_{Si}$ and $E_{LV}(Ni)_{Si}$ are -5.38 kJ/mol and 68.9 kJ/mol, respectively.

Giving the $E_{SL}(Si)_{Ni}$ and $E_{LV}(Si)_{Ni}$ , the solid-liquid interfacial energy and the surface energy of liquid alloy, $\sigma_{SL}$ and $\sigma_{LV}$ , can be expressed as a function of Si content by following equations:

$$\left(\frac{d\sigma_{SL}}{dx_{Si}}\right)_{x_{Si\to 0}} = \left(\frac{RT}{\Omega_M}\right)\left[1 - \exp\left(\frac{-E_{SL}(Si)_{Ni}}{RT}\right)\right] \tag{10}$$

$$\left(\frac{d\sigma_{LV}}{dx_{Si}}\right)_{x_{Si\to 0}} = \left(\frac{RT}{\Omega_M}\right)\left[1 - \exp\left(\frac{-E_{LV}(Si)_{Ni}}{RT}\right)\right] \tag{11}$$

It is clear that the slope of $(d\sigma_{SL}/dx_{Si})_{x_{Si\to 0}}$ or $(d\sigma_{LV}/dx_{Si})_{x_{Si-0}}$ is negative when $E_{SL}(Si)_{Ni}$ or $E_{LV}(Si)_{Ni}$ is negative; whereas, the slope of $(d\sigma_{SL}/dx_{Si})_{x_{Si\to 0}}$ or $(d\sigma_{LV}/dx_{Si})_{x_{Si\to 0}}$ is positive, but very small, if $E_{SL}(Si)_{Ni}$ or $E_{LV}(Si)_{Ni}$ is positive.[35] As for the case of Si infinitely dilute in Ni ( $x_{Si} \to 0$), the increasing Si content reduces the surface energy of liquid, and thus results in the decrease in equilibrium contact angle. As for the case of Ni infinitely dilute in Si ( $x_{Ni} \to 0$ ), the smaller equilibrium contact angle can be mainly attributed to the decrease in interfacial energy with the addition

RSC Advances Accepted Manuscript

RSC Advances Accepted Manuscript

of Ni. Therefore, the equilibrium contact angle does pass through a minimum value, consistent with the experimental results in Fig.4.

Therefore, the Ni/Si ratio (in wt%) plays an important role on the activity of Ni and Si in liquid, the equilibrium contact angle of Ni-Si/C system, the surface energy of liquid as well as solid-liquid interfacial energy. Firstly, the activity of Ni increases with increasing Ni/Si ratio (in Fig.3). Secondly, the equilibrium contact angle decreases with decreasing Ni/Si ratio in the range from 1.2 to 4.0 and increases with decreasing Ni/Si ratio in the range from 0.82 to 1.2 (in Fig.4). As for the case of Si infinitely dilute in Ni, the decreasing Ni/Si ratio reduces the surface energy of liquid, and thus results in the decrease in equilibrium contact angle. As for the case of Ni infinitely dilute in Si, the smaller equilibrium contact angle can be mainly attributed to the decrease in interfacial energy with the increasing Ni/Si ratio (in Fig.5).

## 4. Conclusions

In present work, the reactive wetting of Ni-Si alloys on graphite substrate has been investigated at 1523 K in high vacuum using a modified sessile drop method. A minimum equilibrium contact angle of 20° has been observed in the Ni-45 wt% Si/C system. In addition, the threshold activity of Si in liquid to form SiC at 1523 K is determined to be 0.0173, corresponding for a Si content of 33 at% (19 wt%). Moreover, the effects of Si and Ni on the change of equilibrium contact angle have been analyzed in terms of the adsorption energy, the solid-liquid interfacial energy and the surface energy of liquid alloy. The findings on the effects of Si and Ni on the reactive wetting of Ni-Si alloys on graphite substrate will shed lights onto a better understanding on the nature of reactive wetting systems.

RSC Advances Accepted Manuscript

## Acknowledgments

This work was supported by the program of the National Natural Science Foundation of China (50471007, 51102045). The authors are thankful to the Key Laboratory of Automobile Materials in Jilin University for their kind help in high temperature experiment.

## References

1. W. Barthlott, C. Neinhuis, Planta 1997, **202**, 1-8.

2. T. Zhang, J. Wang, L. Chen, J. Zhai, Y. Song and L. Jang**,** Angew. Chem. Int. Ed**.** 2011**, 50**, 5311–5314.

3. R. P. Evershed, R. Berstan, F. Grew, M. S. Copley, A. J. H. Charmant, E. Barham, H. R. Mottram and G. Brown, Nature**,** 2004**, 432**.

4. Q. Cheng, M. Li, Y. Zheng, B. Su, S. Wang and L. J, Soft Matter 2011,**7,** 5948-5951.

5. Q. Cheng, M. Li, F. Yang, M. Liu, L. Li, S. Wang and L. Jiang, Soft Matter 2012, **8,** 6740-6743.

6. Q. Cheng, L. Jiang and Z. Tang, Acc. chem. res. 2014, **47**, 1256-1266.

7. M. Brochu, M. Pugh and R. A. L. Drew, *Intermetallics* 2004, **12**, 289-294.

8. A. Gauffier, E. Saiz, A. P. Tomsia and P. Y. Hou, *J. Mater. Sci.* 2007, **42**, 9524-9528.

9. J. Xu, X. Liu, M. A. Bright, J. G. Hemrick, V. Sikka and E. Barbero, *Metall. Mater. Trans. A* 2008, **39**, 1382-1391.

10. G. F. Ma, N. Liu, H. F. Zhang, H. Li and Z. Q. Hu, *J. Alloys Compd.* 2008, **456**, 379-383.

RSC Advances Accepted Manuscript

11. R. P. J. Yunes, L. Hong, N. Saha-Chaudhury, R. Bush and V. Sahajwalla, *Isij Int.* 2006, **46**, 1570-1576.

12. T. J. Whalen and A. T. Anderson, *J. Am. Ceram. Soc.* 1975, **58**, 396-399.

13. G. W. Liu, F. Valenza, M. L. Muolo, G. J. Qiao and A. Passerone, *J. Mater. Sci.* 2009, **44**, 5990-5997.

14. O. Dezellus, F. Hodaj and N. Eustathopoulos, *J. Eur. Ceram. Soc.* 2003, **23**, 2797-2803.

15. V. Bougiouri, R. Voytovych, O. Dezellus and N. Eustathopoulos, *J. Mater. Sci.* 2007, **42**, 2016-2023.

16. O. Dezellus and N. Eustathopoulos, *J. Mater. Sci.* 2010, **45**, 4256-4264.

17. A. Ciftja, T. A. Engh and M. Tangstad, *Metall. Mater. Trans. A* 2010, **41**, 3183-3195.

18. B. Drevet and N. Eustathopoulos, *J. Mater. Sci.* 2012, **47**, 8247-8260.

19. Keene and J. B., *Surf. Interface Anal.* 1987, **10**, 367-383.

20. Y. M. Wang and W. Cai, Mater. Sci. Forum. 2015.

21. G. P. Khilya and Y. N. Ivashchenko, Dokl. Akad. Nauk Ukrssr 1973, 69-72.

22. U. Gangopadhyay and P. Wynblatt, *J. Mater. Sci.* 1995, **30**, 94-100.

23. P. Wynblatt, *Acta Mater.* 2000, **48**, 4439-4447.

24. L. Yang, P. Shen, Q. Lin, F. Qiu and Q. Jiang, *Appl. Surf. Sci.* 2011, **257**, 6276-6281.

25. L. Yang, P. Shen, Q. Lin, F. Qiu and Q. Jiang, *Mater. Chem. Phys.* 2010, **124**, 499-503.

26. B.A. Julies, D. Knoesen, R. Pretorius and D. Adams, Thin Solid Films, 1999, **347**, 201-207.
27. Q. Lin and R. Sui, *J. Alloy Compd.* 2013, 274-279.
28. M. Singleton and P. Nash, *J. Phase Equilib. Diff.* 1989, **10**, 121-126.
29. B. Vet, S. Kalogeropoulou and N. Eustathopoulos, *Acta Metall. Mater.* 1993, **41**, 3119-3126.
30. Y. V. Naidich, V. Zhuravlev and N. Krasovskaya, *Mater. Sci. Eng. A* 1998, **245**, 293-299.
31. S. J. Li, X. M. Zang and H. P. Duan, *Key. Eng. Mater.* 2002, **224-226**, 749-754.
32. A. Koltsov, F. Hodaj, N. Eustathopoulos, A. Dezellus and P. Plaindoux, *Scr. Mater.* 2003, **48**, 351-357.
33. J. G. Li, *Compos. Interfaces* 1993, **1**, 37-53.
34. C. Rado, S. Kalogeropoulou and N. Eustathopoulos, *Acta Mater.* 1999, **47**, 461-473.
35. J. G. Li, L. Coudurier and N. Eustathopoulos, *J. Mater. Sci.* 1989, **24**, 1109-1116.
36. C. D., R. I. and E. N., *J. Chim. phys.* 1986, **83**, 561-567.
37. M. Lindholm and S. Bo, *Metall. Mater. Trans. A* 1996, **27**, 2897-2903.

RSC Advances Accepted Manuscript

List of figures

**Fig.1** Wetting process of Ni-35 wt% Si alloy on graphite at 1523 K obtained in vacuum by a modified sessile drop method.

**Fig.2** SEM micrographs of the cross-section of Ni-Si/C systems after held at 1523 K in vacuum for 90min, for (a) Ni-35wt%Si/C system, (b) Ni-45wt%Si/C system, and (c) Ni-55wt%Si/C system. (d) is the magnified image of selected region in (b).

**Fig.3** The activity of Si and Ni for Ni-Si binary system at 1523 K, calculated by Thermo-Calc codes.

**Fig.4** Contact angle versus time for Ni-Si alloys on graphite, measured at 1523 K in vacuum by the modified sessile drop method.

**Fig.5** Variation of （$\sigma_{SL}-\sigma_{SV}$） for NiSi alloys as a function of ln($a_{Ni}$) and ln($a_{Si}$) at 1523 K, calculated based on Fig.3 and Fig.4.

RSC Advances Accepted Manuscript

**Fig.1**

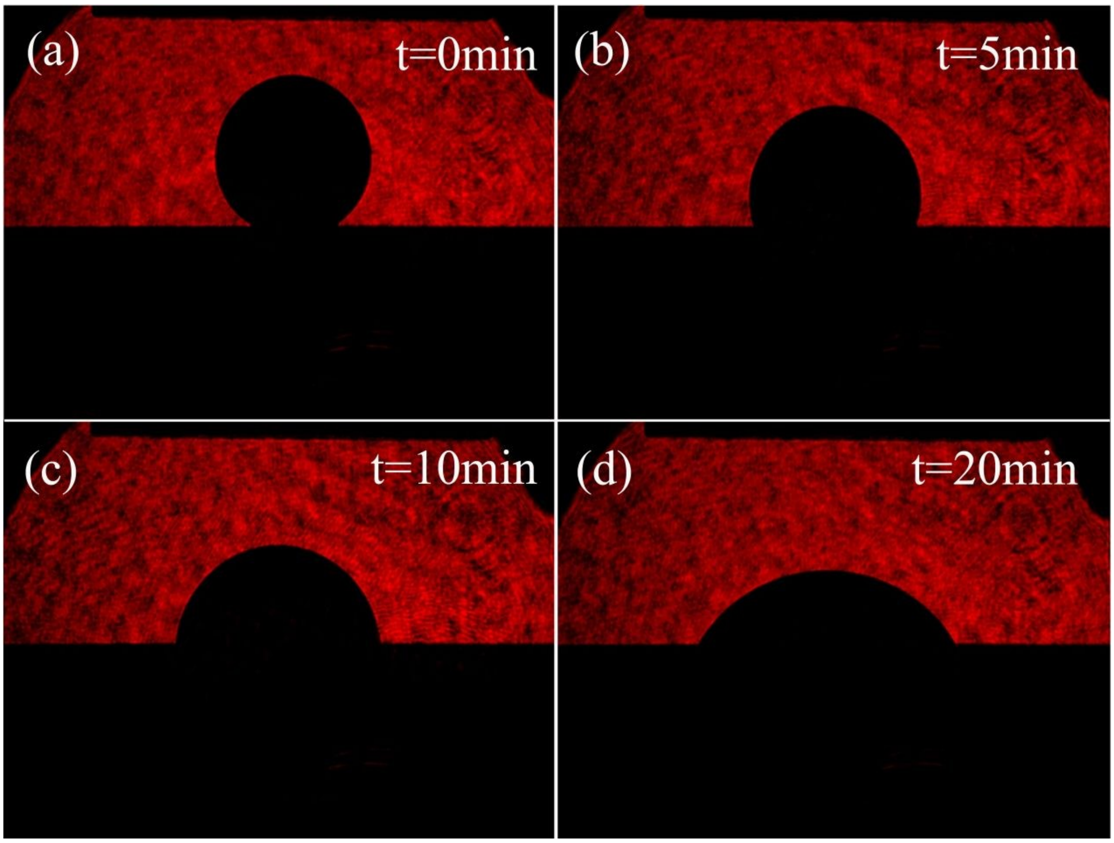


**Fig.1** Wetting process of Ni-35 wt% Si alloy on graphite at 1523 K obtained in vacuum by a modified sessile drop method.

RSC Advances Accepted Manuscript

**Fig.2**

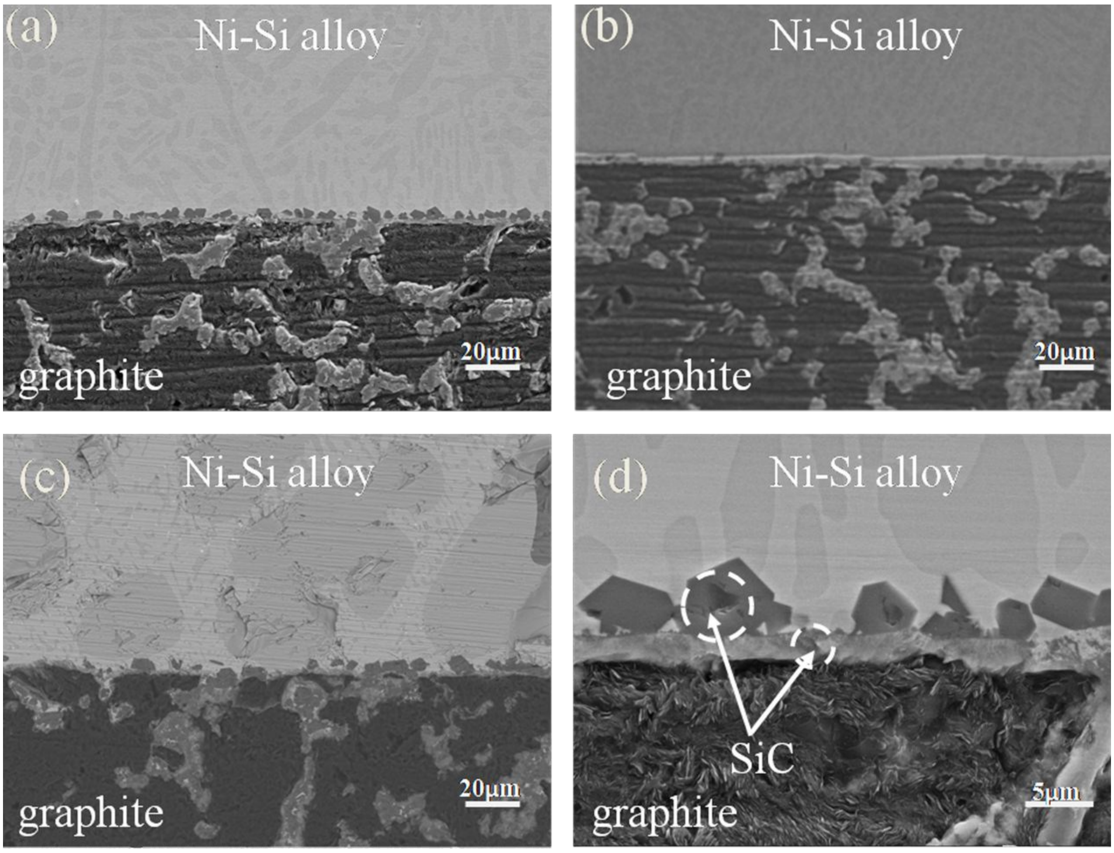


**Fig.2** SEM micrographs of the cross-section of Ni-Si/C systemsafter held at 1523 K in vacuum for 90min, for (a) Ni-35wt%Si/C system, (b) Ni-45wt%Si/C system, and (c) Ni-55wt%Si/C system. (d) is the magnified image of selected region in (b).

RSC Advances Accepted Manuscript

RSC Advances Accepted Manuscript

**Fig .3**

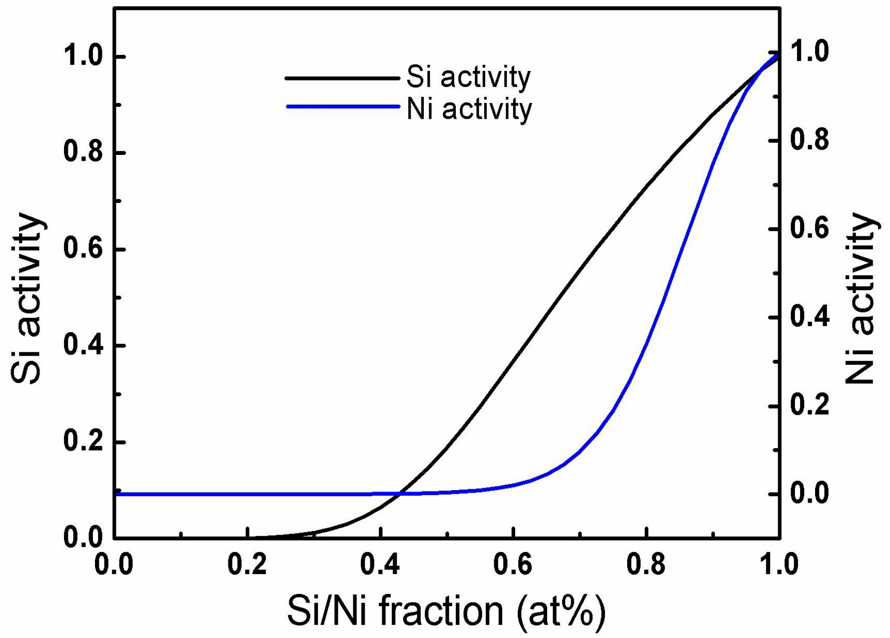


**Fig.3** The activity of Si and Ni for Ni-Si binary system at 1523K,calculated by Thermo-Calc codes.

**Fig.4**

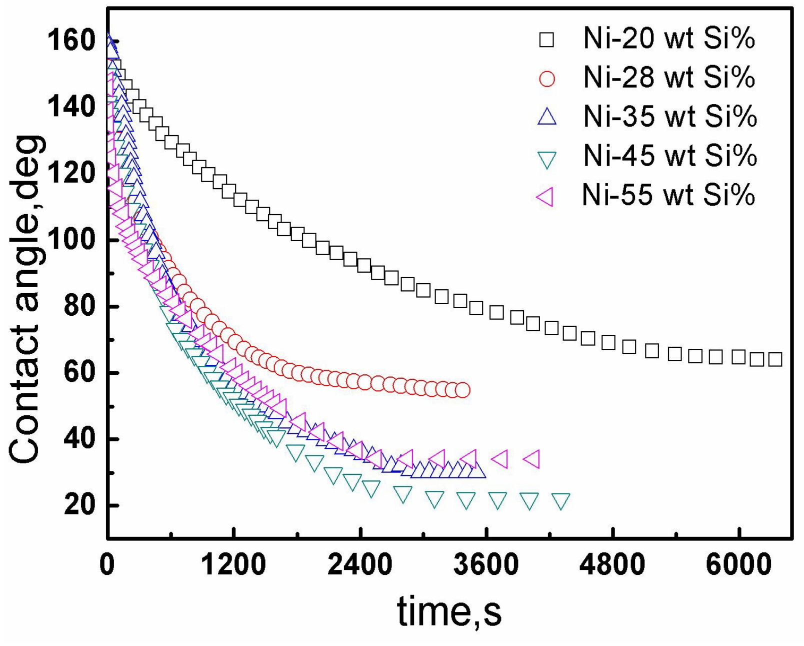


**Fig.4** Contact angle versus time for Ni-Si alloys on graphite, measured at 1523 K in vacuum by the modified sessile drop method.

**Fig.5**

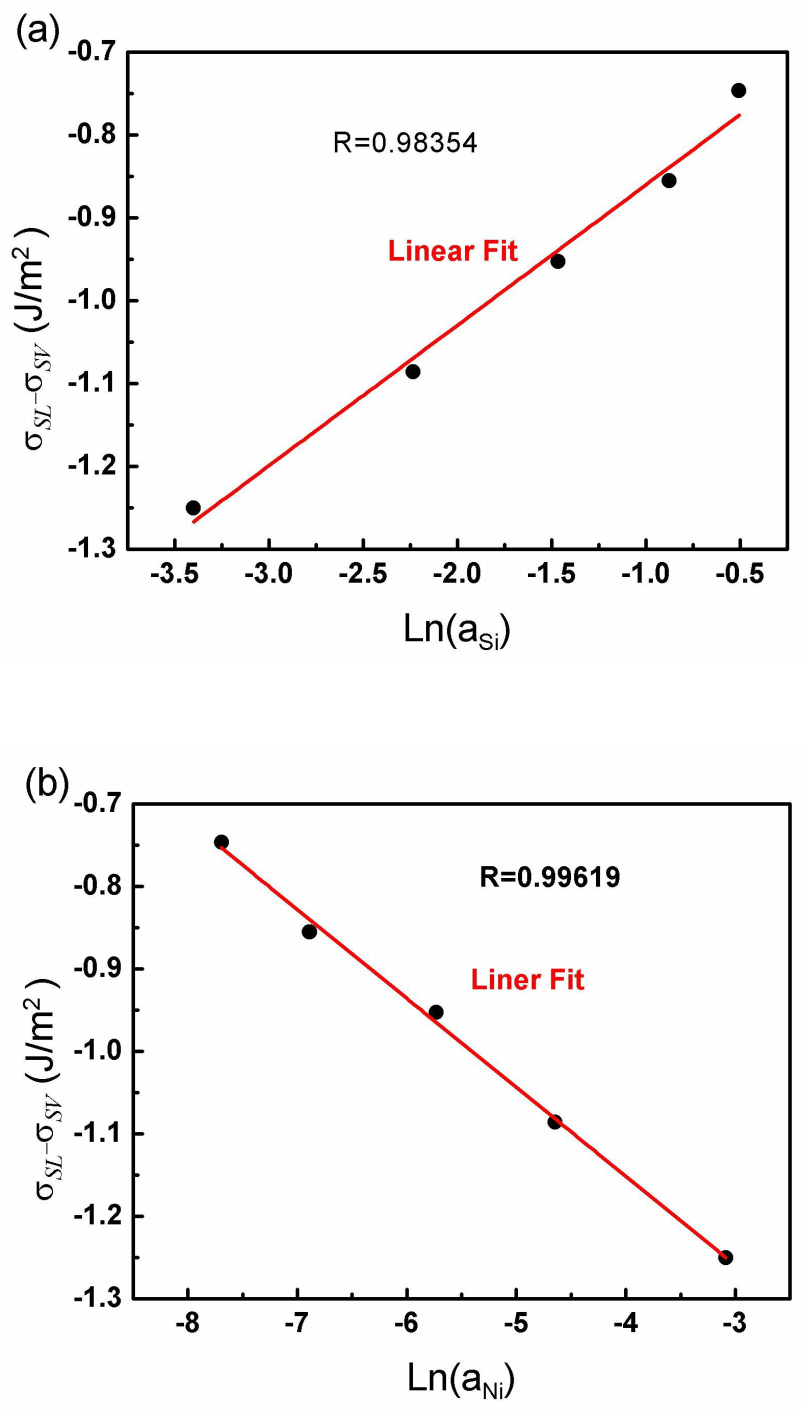


**Fig.5** Variation of （$\sigma_{SL}-\sigma_{SV}$）for NiSi alloys as a function of ln($a_{Ni}$) and ln($a_{Si}$) at 1523 K, calculated based on Fig.3 and Fig.4.

RSC Advances Accepted Manuscript