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Lattice Parameter and Stoichiometry of TiC$_x$ Produced in Alloyed Ti–C Systems by Self-Propagating High-Temperature Synthesis

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Compared with the Ti–C system, the additions of metals (Fe, Al, and Cu) can increase the lattice parameter and stoichiometry of TiC$_x$ by forming metal–Ti intermediate phases (for C/Ti ≤ 0.8). But for C/Ti > 0.8, the Fe addition can decrease the lattice parameter and stoichiometry of TiC$_x$ by the formation of Fe–C solid solutions due to the hindrance of atom diffusion and the decrease of combustion temperature, while the additions of Al and Cu can increase them by the formation of Al–Ti and Cu–Ti solid solutions due to the dilution of Al and Cu.

I. Introduction

IN the past years, TiC$_x$ has been widely produced from mixtures of titanium and carbon powders by self-propagating high-temperature synthesis (SHS) due to its low density and chemical reactivity, and its high hardness, elastic modulus and melting temperature.[1,2] However, the ignition temperature for this reaction is very high, even close to the melting point of titanium. Therefore, the addition of a second metal, such as Ni, Al, Fe, and Cu, is in favor of the decrease of ignition temperature by forming the eutectic liquid at a low temperature or intermetallics with a low melting point to improve the surface reaction rate.[3–7] Nevertheless, most of the research has been focused on the effects of metal additions on the reaction mechanism. According to the Ti–C phase diagram, the composition of TiC$_x$ exists over a wide range of stoichiometry, from $x = 0.47$ to 0.98.[8] It has been demonstrated that the modulus and hardness of TiC$_x$ both decreased as the C/Ti ratio decreased, while the ability of molten metals to wet the carbide increased.[9] Unfortunately, the research on the effects of metal additions on the lattice parameter and the stoichiometry of TiC$_x$ has been relatively limited. Zarrinfar *et al.*,[6] Li *et al.*[7] and Saidi *et al.*[3] investigated the effects of Cu, Al, and Fe addition on the TiC$_x$ lattice parameter, respectively. However, they only provided some interesting experimental results without any explanation of the mechanism. In our recent works,[10] we found that the addition of Ni into Ti–C system could not only increase the lattice parameter and stoichiometry of TiC$_x$ by forming Ni–Ti compounds (for C/Ti ≤ 0.8), but also decrease them (for C/Ti > 0.8) by forming Ni–C solid solution. Thus, there needs to be a good understanding about the effect of the regularity and mechanism of several metal (Al, Fe, and Cu) additions on the lattice parameter and stoichiometry of TiC$_x$.

A knowledge of the parameters that control the stoichiometry of TiC$_x$ from the metal (Fe, Al, and Cu)–Ti–C systems and a method for quick estimation of those are practically very useful in the optimization of both the ease of composite manufacture and their mechanical properties. Therefore, the objective of the present work is to investigate the effect of the regularity and mechanism of several metal (Fe, Al, and Cu) additions on the lattice parameter and stoichiometry of TiC$_x$. It is expected that the present work can serve as a good complement to the companion papers.

II. Experimental Procedure

The starting materials in the present study were made from commercial powders of Al (99.5% purity, ∼29 μm), Cu (99.5% purity, ∼45 μm), Fe (99.5% purity, ∼48 μm), Ti (99.5% purity, ∼25 μm), and C (99.5% purity, carbon black), respectively. A series of experiments were performed, as shown in Table I. The C/Ti molar ratio varied from 0.6 to 1.2 with 40 wt% metals, respectively. The ratios designed in the tables and figures are those of the raw powder mixtures, but not the actual ratio in the SHS products.

Details of the experimental apparatus and procedure were given in a previous article.[11] The compositions in the products were investigated by using an energy-dispersive spectrometer (EDS) (Model Link-ISIS, Oxford, U.K.). The reaction products were identified by powder X-ray diffraction (XRD) (Model D/Max 2500PC Rigaku, Tokoyo, Japan) with CuKα radiation using a scanning speed of 4°/min and a step-scan of $\Delta 2\theta = 0.05°$. Lattice parameter determinations were obtained by using a much slower scanning speed (0.05°/min) performed around the main peaks from 20° to 80° with a step-scan of $\Delta 2\theta = 0.002°$, and the scanning angle was calibrated by using a standard Si wafer.

III. Results and Discussion

Table II shows the XRD patterns of the SHS products with different initial C/Ti ratios, respectively. Some typical XRD patterns of the products are shown in Fig. 1. Clearly, it can be seen that TiC$_x$, metals (Al and Cu) and a small amount of residual C (Al$_4$C$_3$ in the Al–Ti–C system) are detected in the systems with 1.0 and 1.2 C/Ti ratios, while some metal–Ti intermediate phases are detected in the systems with 0.6 and 0.8 C/Ti ratios, as well as TiC$_x$. It is worth noting that no residual C is found in the Fe-Ti-C system with 1.0 and 1.2 C/Ti ratios. To reflect a clearer comparison, the relative molar fractions of some product phase constituents are estimated based on the intensity of TiC (200), Fe$_2$Ti (112), Fe (200), CuTi (110), Cu (111), Al (111), and Al$_3$Ti (112) diffraction peaks,[12,13] as shown in Table II. It is worth noting that only the strongest peaks without overlaying by the peaks of other phases can be used to estimate the relative fraction. From Table II, it can be found that the relative fractions of metal–Ti intermediate phases

Table I. The C/Ti Ratio and Metal Contents of the SHS Reactants

	Series 1			
Metal (Fe, Al, and Cu) contents (wt%)	40	40	40	40
C/Ti ratio	0.6	0.8	1.0	1.2

SHS, self-propagating high-temperature synthesis.

decrease while those of TiC increase with the increase of C/Ti ration from 0.6 to 0.8.

Figure 2(a) shows the function of measured lattice parameter of TiC_x in the Ti–C[10] and metal–Ti–C systems as the C/Ti ratio, respectively. As can be seen, the lattice parameters of TiC_x in all the metal–Ti–C systems increase as the C/Ti ratio increases from 0.6 to 0.8 and from thereon decrease with further increases in the C/Ti ratio. The maximum lattice parameters all appear at 0.8 C/Ti ratio. According to Holt's work, where the relation between the lattice parameter and the C/Ti ratio has been experimentally determined,[14] the actual C/Ti ratios in the products can be established, and the maximum stoichiometry (*x*) also appears at C/Ti = 0.8, correspondingly, as shown in Fig. 2(b). The reason for the appearance of the maximum stoichiometry at C/Ti = 0.8 is the transference of Ti caused by the existence of more metal–Ti intermediate phases in the final products, which has been discussed in our previous study.[9] For ≤0.8 C/Ti ratios, due to the existence of these metal–Ti intermediate phases in the SHS products, the additions of these metals make the actual C/Ti ratios in the TiC_x higher than those in the absence of metals for a given starting ratio of C/Ti. Because the TiC_x lattice parameter is linked to its stoichiometry, the lattice parameters for a given starting ratio of C/Ti in the presence of metals are higher than those in the absence of metals. Furthermore, with the respective increase in the amounts of metal–Ti intermediate phases by the sequence of Cu, Al, and Fe (as shown in Table II), the lattice parameter and stoichiometry of TiC_x from the metal(Cu, Al, and Fe)–Ti–C with ≤0.8 C/Ti ratio increase correspondingly.

In contrast, for >0.8 C/Ti ratios, the additions of different metals result in the different effects about the lattice parameter and stoichiometry of TiC_x. Compared with the lattice parameter of TiC_x in the Ti–C system for a given starting ratio of C/Ti, the additions of Al and Cu increase the TiC_x lattice parameters while the addition of Fe decreases them, as shown in Fig. 2(a). These results suggest that the stoichiometry of TiC_x increases with the additions of Al and Cu, but correspondingly decreases with the addition of Fe, as shown in Fig. 2(b). Similar results

Table II. SHS Product Phase Constituents and Metal Lattice Parameter, as well as Estimated Relative Fractions of Some Phase Constituents

Reactant composition		Product phase constituents identified by XRD and relative molar fractions (mol%) of some phase constituents	Metal lattice parameter (nm)
Metal species	C/Ti		
Al	0.6	38.7 TiC, 44.1 Al₃Ti, 17.2 Al	
Al	0.8	52.8 TiC, 23.5 Al₃Ti, 24.7 Al	
Al	1.0	TiC, Al, C	0.40522
Al	1.2	TiC, Al₄C₃, Al	0.40541
Fe	0.6	25.5 Fe₂Ti, 74.5 TiC	
Fe	0.8	14.3Fe₂ Ti, 79.4 TiC, 6.3Fe	
Fe	1.0	TiC, Fe	0.28725
Fe	1.2	TiC, Fe	0.28782
Cu	0.6	64.1 TiC, 35.9 CuTi	
Cu	0.8	9.2 Cu, 68.1 TiC, 22.7 CuTi	
Cu	1.0	TiC, Cu, C	0.36207
Cu	1.2	TiC, Cu, C	0.36227

SHS, self-propagating high-temperature synthesis; XRD, X-ray diffraction.
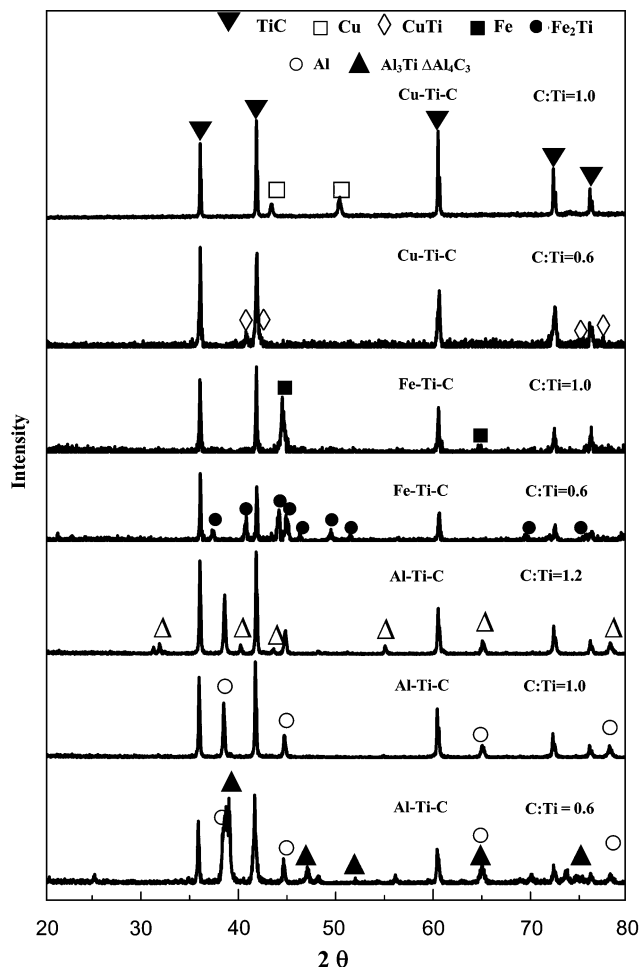
Fig. 1. Some typical X-ray diffraction patterns of the products from the metal–Ti–C systems with different C/Ti ratios.

were also achieved in the Fe–Ti–C system under the thermal-explosion mode of combustion synthesis by Saidi *et al.*[3] Now the question is why the addition of Fe can significantly decrease the lattice parameter of TiC_x in the systems with >0.8 C/Ti ratios while the addition of Al and Cu increases it, because the SHS reactions in these systems are both complete without any metal–Ti intermediate phases. Actually, compared with the Ti–C system, the additions of these metals not only decrease the combustion temperature, but also give rise to the increased diffusion distance, which could give an opportunity for the dissolution of residual Ti or C in these metals and for their retention in solid solution after solidification. For the addition of Fe, the respective dissolution of Ti and C can increase the lattice parameter of Fe. Therefore, the lattice parameters (0.28725 and 0.28782 nm, respectively) of Fe in the SHS products with 1.0 and 1.2 C/Ti ratios in the current study are much higher than that (0.28692 nm) of Fe in the raw materials, respectively, as shown in Table II. However, the solid dissolution of Ti into Fe can increase the C/Ti ratio in the SHS products, which is different from the present results. On the other hand, the substoichiometric TiC_x (*x* < 1.0) formation was more favorable than the stoichiometric one in the reaction of equimolar Ti and C to form TiC_x, and the TiC_x in many reports were substoichiometric,[3,15] which suggested that most of Ti reacted with C to form substoichiometric TiC_x and C might be residual. Especially for the 1.2 C/Ti ratio, more C should be residual. Nevertheless, in the present study, residual C is not detected, implying that it exists in the form of Fe–C solid solution (the solubility of C in Fe is relatively high). In order to verify the formation of Fe–C solid solution, the composition of Fe in the SHS products with 1.0 C/Ti ratio has been determined with EDS. The EDS results indicate that the
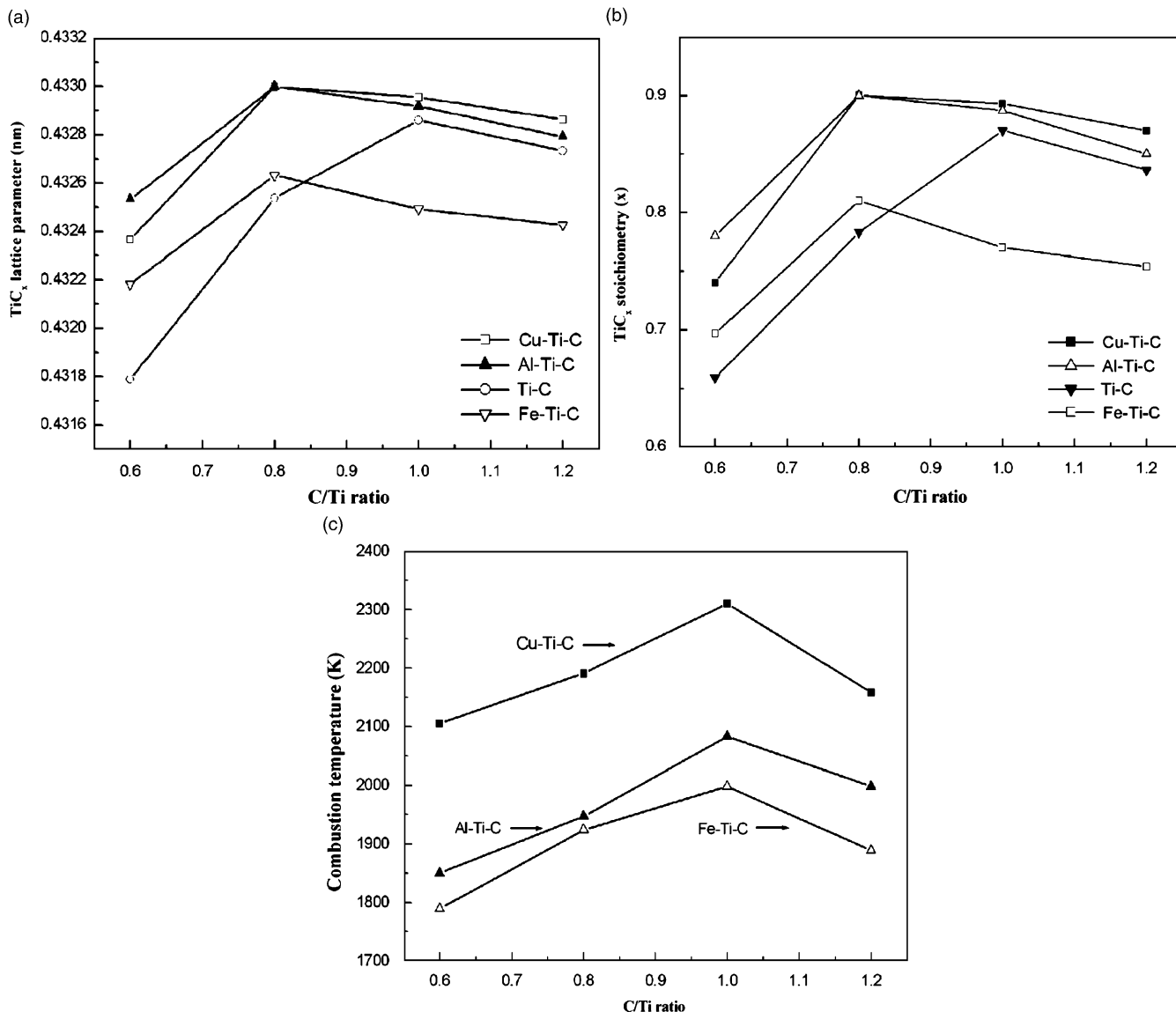
Fig. 2. (a) The lattice parameters of TiC_x, (b) the stoichiometry (x) of TiC_x and (c) the combustion temperatures in the metal–Ti–C systems as a function of the C/Ti ratio.

average atomic ratio of Fe:Ti:C is 88.24:2.32:9.44. As a result, it seems that the solid dissolution of C into Fe plays a more important role in increasing the Fe lattice parameter, which is similar to that in the Ni–Ti–C system.[10]

After the addition of Al and Cu, the combustion temperatures decrease and the diffusion distances between Ti and C atoms increase. Both the respective solid dissolution of Ti and C may occur and can increase the lattice parameters of Al and Cu. Therefore, the lattice parameters of Al and Cu in the SHS products with 1.0 and 1.2 ratios in the current study are much higher than those of Al (0.40506 nm) and Cu (0.36172 nm) in the raw materials, respectively, as shown in Table II. Because the solubility of C in Al and Cu is very low and the reaction is conducted in argon to minimize loss of carbon due to oxidation, some residual C and Al_4C_3 can be found in the final SHS products from Cu–Ti–C and Al–Ti–C systems with 1.0 and 1.2 C/Ti ratios, respectively, as shown in Table II. Considering the difficulties in the transference of C, the solid dissolutions of Ti into Al and Cu are most likely to occur during the SHS process. The EDS results about the compositions of Al and Cu in the products indicate that the average atomic ratio of Al:Ti:C is 91.24:8.39:0.37 and that of Cu:Ti:C is 87.38:12.48:0.14, respectively. As a result, it seems that the solid dissolutions of Ti into Al and Cu play a

more important role in increasing the lattice parameters of Al and Cu. In turn, the transference of Ti caused by the solid dissolution of Ti into Al and Cu can make the lattice parameters and stoichiometry of TiC_x higher than those without the addition of metals, as shown in Figs. 2(a) and (b).

Figure 2(c) shows the variation of the combustion temperatures in the metal–Ti–C systems with the C/Ti ration in the reactants. It is worth noting that the combustion temperature of the Cu–Ti–C reaction systems is higher than those of the Al–Ti–C and Fe–Ti–C reaction systems, because the adiabatic temperature for the 40 wt% Cu–Ti–C system is much higher than those for 40 wt% Al–Ti–C and 40 wt% Fe–Ti–C reaction systems. As indicated, the maximum combustion temperatures increase with the increase in the C/Ti ratio, reaching a maximum value at C/Ti = 1.0, and then slightly decrease at C/Ti = 1.2. For ≤ 0.8 C/Ti ratios, the existence of metal–Ti compounds in the products makes the maximum stoichiometry of TiC_x appear at 0.8. Nevertheless, for a single system, the dependence of the stoichiometry of the yielded TiC_x phase on the C/Ti ratio (for ≥ 1.0 C/Ti ratios) is generally consistent with the behavior of the maximum combustion temperature. The variation trend between the stoichiometry of TiC_x and combustion temperature implies that the temperature might play a crucial role in determining the final

composition of the synthesized TiC_x phase from the complete SHS reaction, and a higher temperature facilitates the atomic diffusion and thus significantly promotes the compositional homogenization.

IV. Conclusion

Compared with the Ti–C system, the additions of metals (Fe, Al, and Cu) can increase the lattice parameters and stoichiometry of TiC_x by forming metal–Ti intermediate phases (for C/Ti ≤ 0.8). But for C/Ti > 0.8, the additions of different metals result in different results: the addition of Fe can decrease the lattice parameter and stoichiometry of TiC_x by the formation of Fe–C solid solutions due to the hindrance of atom diffusion and the decrease in the combustion temperature caused by the dilution of Fe, while the additions of Al and Cu can increase the lattice parameter and stoichiometry of TiC_x by the formation of Al–Ti and Cu–Ti solid solutions due to the dilution of Al and Cu. For all the single complete SHS reactions in the metal–Ti–C systems, the maximum combustion temperature plays a crucial role in the determination of the lattice parameter and stoichiometry of TiC_x.

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