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Title: SYNTHESIS OF (U,Zr)C SOLID SOLUTIONS UNDER EXOTHERMIC CONDITIONS

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### Abstract

The reactions of forming (U,Zr)C solid solutions from their elemental components or similarly less stable reactants such as UC<sub>2</sub> are strongly exothermic due to the high stability of these solid solutions. A simple approach of utilizing this heat of formation energy to assist the solid solution reaction process is to intimately mix the less stable reactant powders and then pressed them into a compact. The compact is then heated to the ignition temperature of the reaction. The feasibility of this reaction method to synthesize (U,Zr)C solid solutions has been demonstrated in this study. The preliminary results also show that both the initial composition and the heating rate have a significant effect on the nature of the reaction process. As expected the degree of powder mixing was also found to affect the completeness of the reaction.

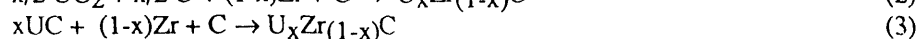
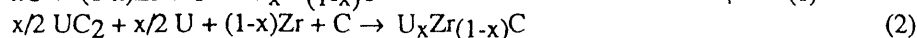
### INTRODUCTION

Proposed manned missions to Mars require nuclear propulsion reactors with high specific impulse in order to reduce the travel time. Mixed uranium-refractory metal carbides such as (U,Zr)C solid solutions are very promising as the fuel for this space application because of their high melting points (up to 3000 °C) and corrosion resistance properties [Butt and Wallace]. Past methods used to synthesize these solid solutions have involved heating mixture compacts of the reactant powders to an elevated temperature and holding at this elevated temperature for an extended period of time. This hold period appears unnecessary considering the high enthalpy of formation of these solid solutions. If the starting powders consist of elemental components or less stable reactant such as UC or UC<sub>2</sub>, the reaction is exothermic enough as illustrated later that it can self propagate, resulting in a combustion type of reaction. The heats of formation in the U-Zr-C system makes it an excellent candidate for the combustion synthesis process which has received much attention as an excellent method for synthesizing refractory materials. The advantages of the combustion synthesis method are discussed in several review papers [Munir 1988, Munir and Tamburini 1989, Subrahmany and Vijayakumar 1992]. In this preliminary study we investigated a variation of combustion synthesis process to synthesize the (U,Zr)C solid solutions. In this method compacts consisting of mixtures of U, Zr, and C powders or mixtures of U, Zr, UC<sub>2</sub>, and C powders are heated in a furnace to a temperature at which the exothermic reaction is initiated and completed in a short time. The objective of this study is to determine the feasibility of forming these (U,Zr)C solid solutions using this exothermic process. This investigation also examines the effects of starting powder compositions and the rate of heating.

### ADIABATIC COMBUSTION TEMPERATURE

In a powder compact, when the reaction between the reactant particles is sufficiently exothermic and the heat generated is retained to heat the next layer of the reactants, the reaction can self propagate in a form of combustion wave until the reactants are consumed. This propensity to self propagate can be assessed from the value of the adiabatic combustion temperature of the reaction. The adiabatic combustion temperature is the highest temperature the reaction system can achieve without any heat loss to the environment and can be calculated from tabulated thermodynamic data.

Three reactions of interest to this study are



where  $x$  varies from 0 to 1. The adiabatic combustion temperature ( $T_{ad}$ ) can be calculated from

$$\Delta H_{298}^0 = \int_{298}^{T_{ad}} C_p dt \quad (4)$$

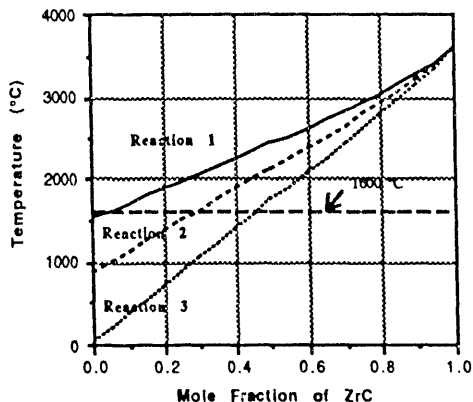
where  $\Delta H_{298}^0$  is the enthalpy of the reaction for forming  $U_xZr_{(1-x)}C$  at 298 K, and  $C_p$  is the heat capacity of the products. The enthalpies of reaction for the three above reactions are different due to different starting reactants and are calculated by subtracting the sum of the enthalpies of formation of the reactants from the enthalpy of formation of the product. To circumvent the lack of published data, the heat capacities are estimated by applying the Neumann-Kopp rule and the enthalpies of formation of the various  $U_xZr_{(1-x)}C$  compositions by assuming that ZrC and UC form ideal solution using the basic thermodynamic data shown in Table 1.

TABLE 1. Thermodynamic Data\*

Phase	$C_p(\text{J/mole}) = a + bT + cT^{-2} + dT^2 + eT^3$					$\Delta H_{f-298}^0$ (KJ/mole)
	a	$b \times 10^3$	$c \times 10^{-5}$	$d \times 10^6$	$e \times 10^8$	
ZrC	51.13	3.39	-12.97	--	--	207.1
UC	50.96	25.72	6.19	-18.68	57.17	97.5
UC <sub>2</sub>	--	--	--	--	--	88.3

\* Data from [Kubaschewski et al 1993] except  $C_p$  of UC from [Holley 1984].

The detailed steps of calculating  $T_{ad}$  is elucidated elsewhere [Munir 1988], and it has been empirically determined that for a solid-solid reaction system to be self-sustaining,  $T_{ad}$  needs to be  $> 1600$  °C. The calculated results, assuming the final product is solid at  $T_{ad}$ , are shown in Figure 1. In general  $T_{ad}$  increases as the composition moves toward the ZrC rich side. It can be seen in Table 1 that the formation reaction of ZrC is significantly more exothermic than that of UC, see Table 1, and therefore the energy release from the bond formation between Zr and C is the major heat source for raising the reaction temperature. It can be seen in Figure 1 that nearly all compositions of Reaction 1 can potentially self propagate, while in the case of Reaction 2 that condition is true for composition with the ZrC mole fraction greater than 0.3 and in the case of Reaction 3 for ZrC mole fraction greater than 0.45. The more exothermic Reactions 1 and 2 were investigated in this study.



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FIGURE 1. Calculated adiabatic combustion temperature as a function of ZrC mole fraction

## EXPERIMENTAL METHOD

The reactants used in this study were depleted uranium powder (-325 mesh), zirconium powder (-325 mesh), graphite powder (-325 mesh), and UC<sub>2</sub> powder (-325 mesh). All the sample preparation and reaction experiments were done in glove boxes under argon atmosphere. The powder mixtures were prepared by weighing out appropriate amounts of the powders according to the stoichiometry of the final product to be synthesized, Table 2,

and then ball milled for 16 hours. The last mixture was prepared by hand blending for about 10 minutes the appropriate amounts of Mixtures M2 and M4 to make up the desired composition. With the exception of the Mixture M4 (Zr+C), all other mixtures required 0.5 wt% of binder (equal weight parts of poly glycol and steric acid) added in order to form an intact compacts. These cylindrical compacts had a diameter of 1.42 cm, a height ranging from 1.19 to 1.59 cm and a bulk density ranging from about 55 to 70 % of the theoretical density. A 1/8" (0.318 cm) hole was drilled axially from the center of one end of the compact to about half the height of the sample to allow for placement of a thermocouple.

TABLE 2. Mixtures and Heating Rates Studied

Mixture ID	Starting Composition (wt%)				Nominal Formula ( $U_xZr_{1-x}C_z$ )			Heating Rate ( $^{\circ}C/min$ )	Expected Product Phases	
	UC <sub>1.92</sub>	U	Zr	C	x	1-x	z			
M1	37.1	33.7	25.8	3.4	0.50	0.50	1.00	30	single solid solution	
M2	0.0	67.8	26.0	6.2	0.50	0.50	0.91	30, 100	single solid solution	
M3	23.9	0.0	66.3	9.8	0.11	0.89	1.22	30	solid solution and C	
M5	0.0	36.0	55.2	8.8	0.20	0.80	0.96	100	single solid solution	
M4	0.0	0.0	88.4	11.6	0.00	1.00	1.00	30, 100	ZrC	

The compacts were heated in a resistance heating furnace under a vacuum of  $< 10^{-4}$  torr. One of the two thermocouples (W-5%Re/W-26%Re type, 1/8" molybdenum sheath diameter) inside of the furnace was inserted into the sample to measure the sample temperature; while the other thermocouple outside of the sample was used for the furnace temperature control. All samples were heated at 30  $^{\circ}C/min$  to 500  $^{\circ}C$  and held for 10 to 30 minutes to outgas or burn off the binder. After this outgas stage, the sample was heated up at a rate indicated in Table 2 to 2000  $^{\circ}C$ , above the melting point of Zr (1852  $^{\circ}C$ ). The temperatures were recorded on a chart recorder. The reacted samples were analyzed by x-ray diffraction and examined in both optical and scanning electron microscopes.

## RESULTS

Only the M4 samples heated at 30 and 100  $^{\circ}C/min$  and the M2 sample heated at 100  $^{\circ}C/min$  showed noticeable exothermic effects, Figure 2, while all the other samples show no noticeable temperature deviation from that of the furnace. In both the M4 samples heated at 30 and 100  $^{\circ}C/min$ , the exothermic effect was observed to initiate at about 1760  $^{\circ}C$  which is about 100  $^{\circ}C$  lower than the melting point of Zr (1852  $^{\circ}C$ ). The temperature rise was

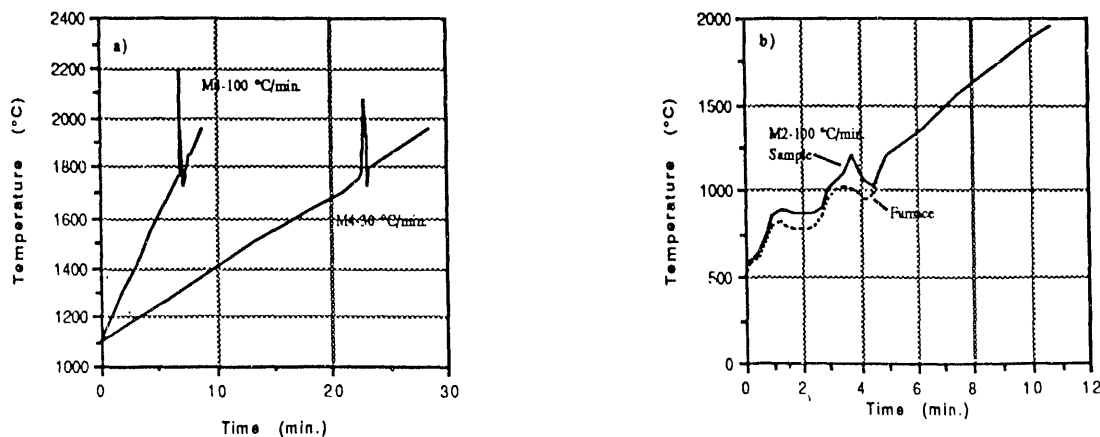


FIGURE 2. Measured sample temperature with time: a) the M4 samples and b) the M2 sample.

significantly higher in the 100°C/min run than in the 30 °C/min run. For the 100°C/min run the maximum temperature reached above 2200 °C, the maximum temperature that could be recorded by the chart recorder, while for the 30 °C/min run the maximum temperature measured was 2050 °C. A sample temperature which drops below the general linear rise after the occurrence of the exothermic peak is an effect resulting from the furnace temperature control. Since the control thermocouple also picked up some heat from the reaction, this caused a momentary decrease in power input to the furnace, resulting momentary cooling of the furnace. The exothermic effect in the case of the M2 sample heated at 100 °C/min is less conspicuous ( see Figure 2b) but occurred at about 1050 °C, which is about 80 °C lower than the melting point of uranium (1132 °C). A temperature rise of about 125 °C was observed. The oscillation observed in the temperatures traces of this case is an effect of furnace control which had not been optimally tuned in this temperature range. Other than pressure increase due to binder burn off in the low temperature range ( $\leq 500$  °C), no noticeable change in furnace pressure was observed during the experimental runs.

In general the reacted samples appeared lighter in color from the original dark gray to medium gray, and had some increase in volume. The cylindrical shape was generally retained. Some laminations and cracks were observed in some samples, but not in the M4 samples which had no binder addition. The reacted M4 samples were also most sintered, while the reacted M3 sample which contained the greatest amount of carbon was most friable.

The x-ray diffraction patterns of six reacted samples along with that of the starting UC<sub>2</sub> powder are presented in Figure 3. These patterns exhibit definite solid solution formation in most cases. The M2 samples (30 and 100 °C/min runs) show to have formed a single solid solution phase, while that of the M1 sample has formed two solid solutions, the M3 sample also has two basic solid solution phases, and the M5 sample contains the two basic binary carbides ( ZrC and UC) and minor amounts of variable composition solid solutions. The M4 sample as expected formed only ZrC phase. There were two unidentified peaks (at about 21 and 24 ° two theta) which are present in all cases and even in the starting UC<sub>2</sub> powder. They were later found to be from the Mylar film used to cover the x-ray powder samples. In the M3 sample, there are minor amounts of UC<sub>2</sub> and C. The lattice parameters of the main solid solutions in the reacted samples are presented in Table 3. Assuming ideal solution so that the lattice parameters follow the Vegard rule, the mole fractions of ZrC<sub>0.96</sub> in the solid solutions are calculated for each case and presented Table 3.

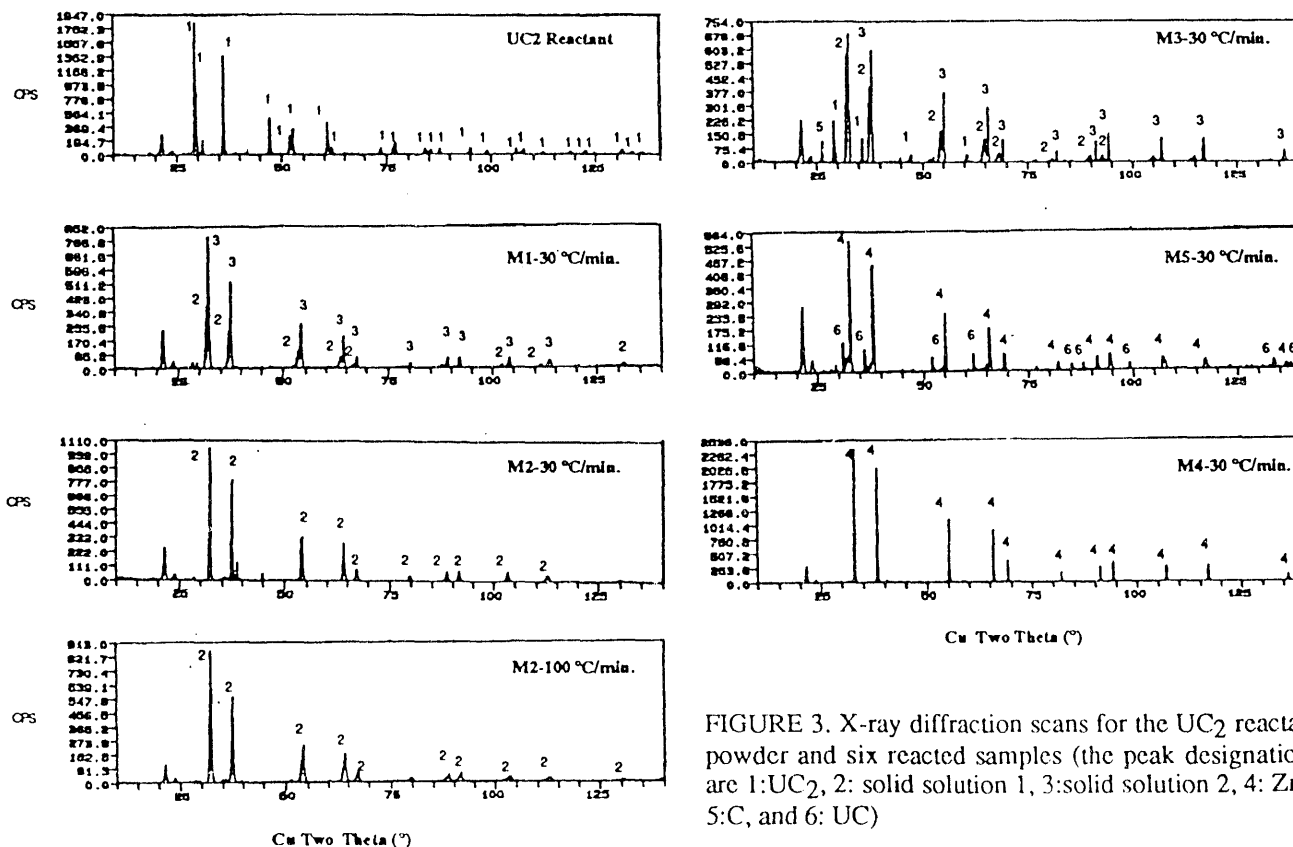


FIGURE 3. X-ray diffraction scans for the UC<sub>2</sub> reactant powder and six reacted samples (the peak designations are 1:UC<sub>2</sub>, 2: solid solution 1, 3:solid solution 2, 4: ZrC, 5:C, and 6: UC)



Table 3: The Lattice Parameters of the Product Solid Solutions\*

Sample	Lattice Parameter (Å)		Calculated ZrC <sub>0.96</sub> mole fraction	
	a <sub>1</sub>	a <sub>2</sub>	Solid Solution 1	Solid Solution 2
M1-30 °C/min.	4.847	4.793	0.43	0.64
M2-30 °C/min.	4.806		0.59	
M2-100 °C/min.	4.804		0.60	
M3-30 °C/min.	4.782	4.720	0.68	0.92
M5-30 °C/min.	4.961	4.696	0.00	1.00
M4-30 °C/min.	4.697		1.00	

\* The lattice parameters of UC<sub>1.0</sub> and ZrC<sub>0.96</sub> are 4.960 and 4.698 Å, respectively [Storms 1967].

Microstructural examination was performed on the longitudinal cross sections of the reacted samples. Since it was difficult to prepare representative surfaces of the reacted M1 and M3 samples due to particle fall out, only the M2, M4 (30 °C/min.) and M5 samples were examined in detail. As seen in the optical micrograph in Figure 4, the reacted M4 sample exhibits a rather porous yet connected microstructure. Generally a single ZrC phase was found in the sample except in the region around the thermocouple hole where two phases were found. The second phase, shown as the light color phase in Figure 4, contains Mo but no Zr as revealed by the x-ray energy dispersive spectrum (XEDS) analysis performed in a SEM. This finding indicates that the sample interacted with the Mo sheath of the thermocouple. From the appearance of the microstructure, the Mo phase appeared to have melted and subsequently intermixed with the Zr-C mixture. Since the melting point of Mo is 2610 °C, the actual reaction temperature was probably much higher than the measured maximum reaction temperature (2050 °C). Although carbon could not be detected with the XEDS, it is likely the Mo containing phase is a carbide phase. The M2 sample was also found to have a major phase identified by the XEDS analysis to contain both uranium and zirconium. This phase corresponds to the solid solution found in the x-ray diffraction analysis. The M2 sample also contains a minor secondary phase which has uranium but no zirconium, Figure 5. This secondary phase was most evident in the region near the exterior surfaces and around the thermocouple holes where heat loss is expected to be greater. The amount of this uranium-containing phase (either a uranium carbide or pure uranium) was below the detection limit of the x-ray diffraction analysis. In the case of the M5 sample, the microstructure is rather heterogeneous, Figure 6, and at least three phases were observed: a zirconium containing phase, a phase containing variable amounts of uranium and zirconium, and a uranium containing phase. These three phases correspond to ZrC, variable (U,Zr)C solid solution, and UC as identified by x-ray diffraction, Figure 3.

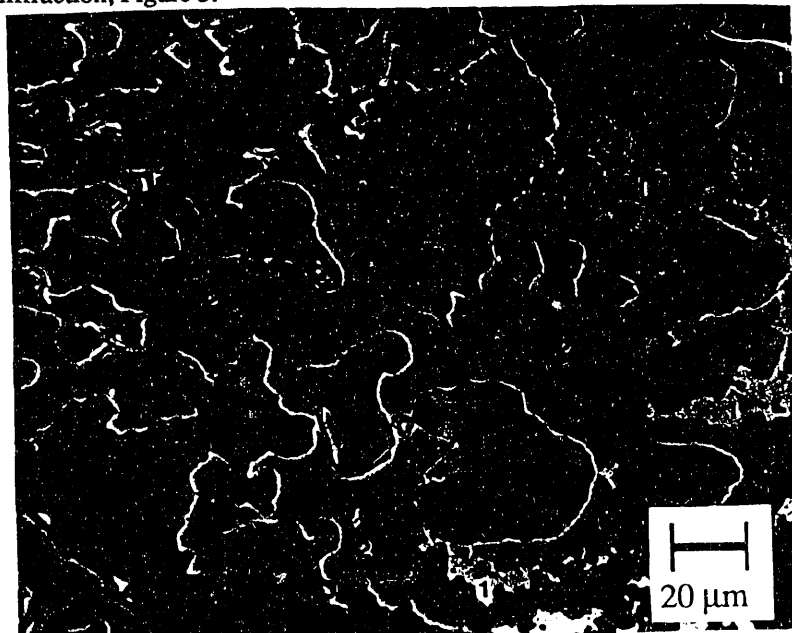


FIGURE 4. Optical micrograph of the M4-30 °C/min. sample (1: molybdenum containing phase, 2: ZrC phase).

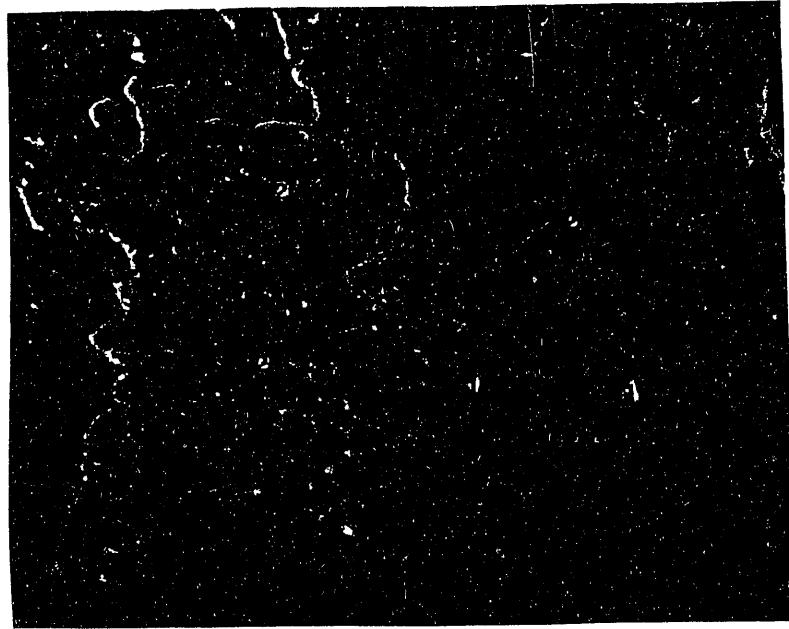


FIGURE 5. Optical micrograph of the M2-30 °C/min. sample (1: uranium containing phase, 2: (U,Zr)C solid solution.)

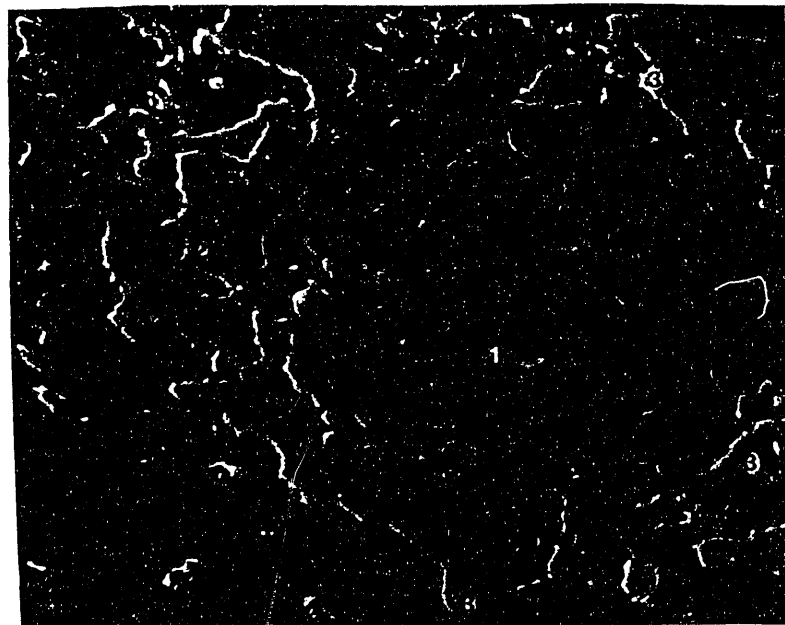


FIGURE 6. Optical micrograph of the M5-30 °C/min. sample (1: ZrC, 2: variable composition (U,Zr)C solid solution, 3: UC)

## DISCUSSION

From the results obtained in this preliminary study, the onset of the combustion reaction was found to depend on the lowest melting point of the reactants and the relative amount of this low melting point reactant. When uranium, which has the lowest melting point among the reactants used, is present in a substantial amount, the initiation of the exotherm was observed near the melting point of the uranium as in the case of the M2 sample heated at 100 °C/min. When uranium was absent, as in the case of the M4 samples, the onset shifts toward the melting point of zirconium which is higher than that of uranium. That the presence of liquid facilitates the exothermic reaction can be explained by the higher diffusion and dissolution rates in liquid state. This results in more reactant atoms available for reaction at a given time. The higher reaction rate subsequently releases more energy which raises the temperature of the reaction system and further increases the reaction rate. Under this condition the entire reaction process of the sample can be completed in a very short time. If no heat is lost to the environment, the temperature of sample can rise to its adiabatic combustion temperature. This rapid rise in temperature is especially evident in the highly exothermic M4 samples (the Zr+C mixture).

The external heating rate has a significant effect on how the exothermic reaction proceeds in an all-solid reactant system. As a sample of this type of system is being heated up to temperatures below the first liquid formation temperature, solid diffusional reactions occur at the contact regions between the reactant particles. These diffusional reactions can form intermediate product phases at these contact regions. At a low external heating rate, the sample spends more time at temperatures for solid diffusion to occur, and substantial amounts of intermediate product phases can form. The formation of intermediate phases have been observed in other exothermic solid reactant systems [Wang et al 1990]. The formation of intermediate products not only reduces the available thermodynamic driving force for subsequent combustion reaction triggered by the presence of liquid [Wang et al., 1990], but can also form diffusional barriers between reactant atoms. Higher heating rate reduces the amount of intermediate solid product phases formed from solid-diffusional reactions. This results in greater amounts of initial reactants available for the accelerated exothermic reaction when the first liquid formation temperature is reached. This effect manifested by an exothermic peak was seen in the case of the M2 sample heated at 100 °C/min. but not in the 30 °C/min case. In both cases, the reacted samples formed practically the same amount of the expected product, see Figure 3. This fact indicates that the reaction of the 30 °C/min. sample occurred at a lower rate but completed over a longer period of time, while the reaction of the 100 °C/min. sample occurred at a higher rate but completed over a shorter period of time. In this study, many of the other samples heated at 30 °C/min. also did not show detectable exothermic effect; this however does not indicate absence of exothermic reactions during the heat up process. In all cases, the results of x-ray phase analysis show that reactions to form solid solution and/or carbides have occurred. These exothermic reactions apparently occurred at such a low rate such that the 1/8" diameter thermocouple with a relatively large thermal mass is not sensitive enough to detect the temperature change.

The solid solutions are more easily formed from compositions containing elemental U, Zr, and C powders. While UC<sub>2</sub> is a more readily obtainable reactant but is a less desirable starting reactant because of its higher melting point (2450-2480°C) and the lower thermal effects of samples, Figure 1. As shown in both the M3 and M1 samples which started with uranium contained in UC<sub>2</sub>, the reaction actually resulted in two partial solid solution phases, Figure 3 and Table 3, rather than a single solid solution expected.

Finally, the effect of inadequate mixing is demonstrated in the M5 sample which was prepared by hand blending appropriate amounts of M2 and M4. Although this sample is expected to more easily form a single solid solution than M2 due to a higher enthalpy of reaction, the reacted product showed incomplete reaction and contains mostly ZrC and minor amounts of UC and (U,Zr)C solid solutions. The microstructure also exhibited a rather heterogeneous distribution of these phases. This leads to the conclusion that mixing is an important factor in preparing powder reactants for this reaction process.

## CONCLUSION

This preliminary study has demonstrated the feasibility of synthesizing (U,Zr)C solid solutions starting with U, UC<sub>2</sub>, Zr and C reactant powders under combustion conditions. The UC<sub>2</sub> has a higher melting point and contributes less reaction enthalpy, and so is less capable of achieving complete reaction in the bulk sample. Our results also show that the initial composition and the heating rate have a significant effect on the nature of the reaction process. As expected the degree of powder mixing also affects the completeness of the reaction in the bulk sample.

### Acknowledgment

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