

IIM - G. D. Birla Gold Medal Lecture

By Dr Raghvendra Tewari



Shri G.D. Birla

A great leader, Shri G. D. Birla was a reformer, an industrialist, and above all a nationalist. Known for his entrepreneurial spirit and considered a doyen of Indian industry, he laid the foundation of the Birla empire. As a visionary businessman, Shri G.D. Birla has gone down in Indian history as the creator of one of India's largest industrial conglomerates.

Raised in Pilani and Calcutta (now Kolkata), Shri. G.D. Birla forayed into business during World War I. Known for his farsightedness, he was highly vocal about his support towards domestic enterprise and his distaste for foreign capital and foreign goods. He endeavoured to substitute foreign textiles with home-made cloth using the best technology available.

In 1925, along with a group of pioneering industrialists, he set up the Indian Chamber of Commerce, which was closely associated with the Indian Freedom Movement, as the first organised voice of indigenous Indian industry. With Sir Purshottamdas Thakurdas, he co-founded the Federation of Indian Chambers of Commerce and Industry (FICCI). He represented India at the first and second Round Table

conferences in London along with Mahatma Gandhi. In 1945, he was one of the authors of the economic development plan known as the Bombay Plan, a major private sector initiative. The period between 1921 and 1945 was one of the most crucial in Shri G.D. Birla's career, establishing him as the foremost industrialist of pre- independence India.

Shri G.D. Birla wholeheartedly believed in giving. He supported the freedom struggle financially to fulfil the dream of millions of Indians of an independent India. He was also a great believer in the power of education. In 1929, under Birla Education Trust, he set up a primary school focusing on the development of education in Rajasthan. In the 1940s, at the behest of Sardar Vallabhbhai Patel, Shri G.D. Birla contributed to establish the Birla Vishwakarma Mahavidyalaya College in Baroda (now Vadodara). He also contributed for Aligarh Muslim University and helped in setting up the Banaras Hindu University.

Shri. G. D. Birla helped shape the educational trajectory of the country. One of the institutions he founded was the prestigious Birla Institute of Technology and Sciences (BITS), Pilani. A Padma Vibhushan awardee, he also played an instrumental role in setting up several temples, planetariums and hospitals across India.

The G D Birla Gold Medal was established in 1985 in his honour.

Niobium Alloy System: An underutilized Saga

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In my research career of 34 years, I have worked on many alloys and materials. Fascinating field of materials characterization and microscopy has always attracted me to develop new materials, find out underlying mechanisms and provide solutions to unresolvable problems. Among various material, niobium-based alloys because of their unique properties have drawn my attention. Today I devote my presentation to this wonderful but underutilized and one of the least studied alloy systems. In addition, this will be my tribute to my guide Late Dr. Srikumar Banerjee, as this idea of starting research work on Nb based alloys has given necessary driving force for the work.

Among the five elements, which are commonly referred as refractory metals, Nb metal stands out because of its applicability in widest temperature range spanning from 4K as superconductor to 1400 K as structural material. By virtue of these peculiar properties Nb has always been a part of materials development program of Department of Atomic Energy (DAE). The present talk is mainly devoted to the development of niobium and its alloys for various applications. However, to provide a wider prospective, other refractory metals have also been included.

Refractory metals (V, Nb, Ta, W, Re) and their alloys are capable of meeting an aggressive environment with respect to radiation, temperature, corrosion (gaseous and liquid metal) and stress for prolonged periods. These materials can therefore cater to high temperature structural materials for new generation nuclear reactors like accelerator driven systems, compact high temperature reactors (CHTR), advanced heavy water reactor fusion devices and space shuttles, aerospace structures, jet engine materials and furnace heating and shielding elements [1]. These metals are also used in many other varieties of applications. They are extensively used as alloying metals in steel industries, sintered carbide tools in the form of respective ferroalloys and carbides and many more. Specific application such as that of niobium in the field of metallic superconductor and nuclear reactor, tantalum as miniature capacitor and tungsten as incandescent filament, molybdenum as heating element and cathode support and rhenium as alloy softener bestowed them prominent recognition. Among the various activities carried out in the

Niobium for superconducting cavities

Niobium, among all refractory metal, has lowest melting temperature, lowest density, and lowest room temperature elastic modulus. Nb becomes superconductor at cryogenic temperatures. At atmospheric pressure, it has the highest critical temperature of the elemental superconductors at 9.2 K. Niobium has the greatest magnetic penetration depth of any element. In addition, it is one of the three elemental type II superconductors, along with vanadium and technetium. Low temperature applications include superconducting cavities; tunnel barrier/ Josephson junctions in nano-electronic device; wires for superconducting magnets in the form of niobium-tin and niobium-titanium alloys.

From the DAE prospective, high performance superconducting radio frequency (SRF) cavities are crucial for the development of high energy and high duty factor superconducting LINACS required for future pulsed spallation neutron sources and accelerator driven sub-critical sources [2]. High purity Nb is an ideal choice for such SRF cavities. The performance of these SRF cavities is measured in terms of its quality factor (Q_o) and accelerating gradient (E_{acc} in MV/m). Q_o is inversely related to the surface resistance of the cavity and needs to be maximized to a value greater than 10^{10} . In order to improve Q_o , fabrication and processing of the cavities is carried out in very stringently controlled processes of thermal and electro-chemical treatments. Despite such careful preparations, performances of such cavities are many a times below the theoretical limit and repeatability of the quality is not easily achievable. Hence, the SRF community continuously strives to evolve these processing parameters. One of the most essential steps towards the improvement of Q_o is related to the reduction of ingress of bulk hydrogen during high vacuum and high temperature degassing (HVTG) processes. The basic idea behind these efforts is to achieve a combined optimization of Q_o and E_{acc} . However, the real success of such thermal treatments would only be realized when all the treatments after the degassing cycle are eliminated and for this, various aspects associated with the vacuum degassing treatments should be understood.

In DAE, consolidated efforts have been made to reproducibility produce high performance cavities by systematically studying the ingress of various interstitial impurities by combining transmission electron microscopy and time of flight secondary ion mass spectrometry. It was unequivocally established that upon annealing under vacuum though Nb_2O_5 decomposed

quickly, other sub-oxides like NbO remained stable up to high temperature. Role of other impurities like, carbon, sulphur and nitrogen in the hydrogen degassing was elucidated (Fig.1) [3]. A proposed mechanism was used to modified the treatment of the cavities which has been successfully demonstrated in producing high quality cavities being transferred to US national labs to be integrated with the accelerators (Fig.2).

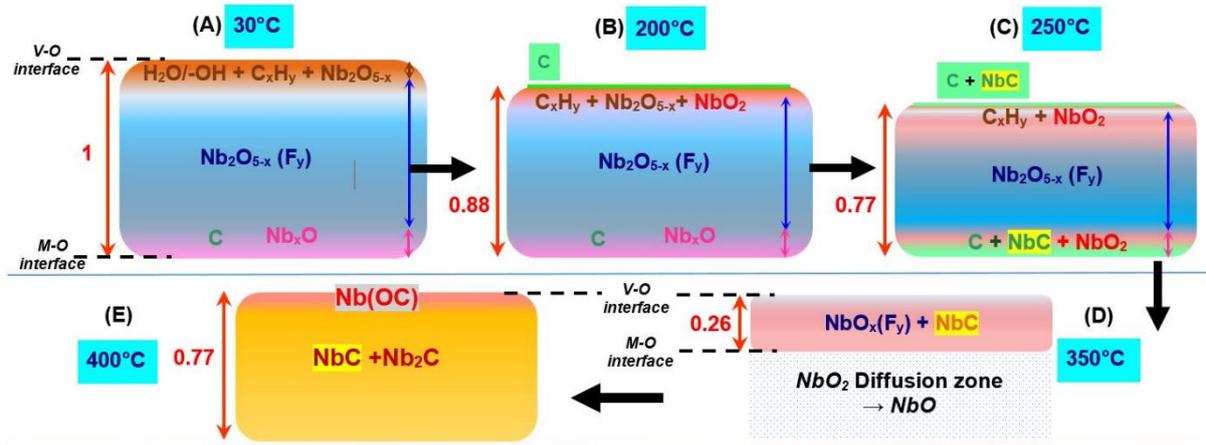


Fig. 1 Schematic representation of the reduction of oxide layer under vacuum upon heating.



Fig.2 Vacuum cavities prepared in DAE and provide US national labs for accelerators.

Nb-Alloys for Compact high temperature reactors

Alloys of Nb have a good combination of high temperature strength, chemical compatibility with most liquid metals, easy fabricability, lower density and stability in nuclear environments. The strength of pure Nb is, however, known to decrease substantially

above 1000°C. Various approaches have been used to improve the strength of Nb at elevated temperature. One of the best approaches to increase the strength of Nb alloys is by adding Zr and C to Nb by solid solution strengthening and precipitation hardening respectively.

Existing literature on the Nb alloy shows that deformation temperatures for the alloys are as high as ~1600°C and the recrystallization temperature as ~1480°C. This demands for the exploration of a new alternative route for deformation as well as recrystallization of the Nb alloy at lower temperatures which would make the fabricability of the alloy suitable with the existing facilities in DAE. For this purpose, Nb-Zr-C alloys were electron beam melted under high vacuum conditions which was followed by vacuum arc remelting to refine the grain-size. Preparation of the alloy needed special attention, as prior melting of Nb entire C would react with available traces of oxygen in the system and convert into gaseous form. Fig.3 shows a flow sheet for the preparation of Nb alloy to achieve the desired alloy composition as Nb- 1% Zr and 0.1%C [4]. Vacuum arc melting which followed EB melting, the brought desirable homogeneity to the alloy. Next problem of refractory metal alloys is the requirement of high processing temperatures and prone to oxidation at these elevated temperatures. To address both the issues formability of the Nb-1Zr-0.1C alloy was addressed by a series of compression tests at different temperatures ranging from 800 to 1300°C at different strain rates up to 35% deformation (Fig.4). The flow stress of the alloy remains above 200 MPa up to 1300°C. However, in between temperature range from 600-800°C the flow stress suddenly dropped from 268 MPa to 241 and subsequently increased again up to 290 MPa. This provided a window of operation at temperatures close to 800°C [4,5].

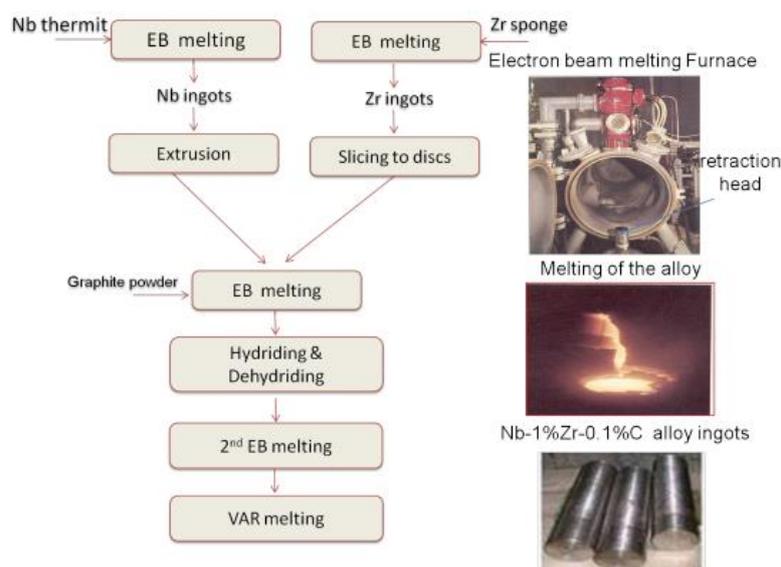


Fig. 3 Flow sheet for the preparation of Nb-1%Zr-0.1%C alloy.

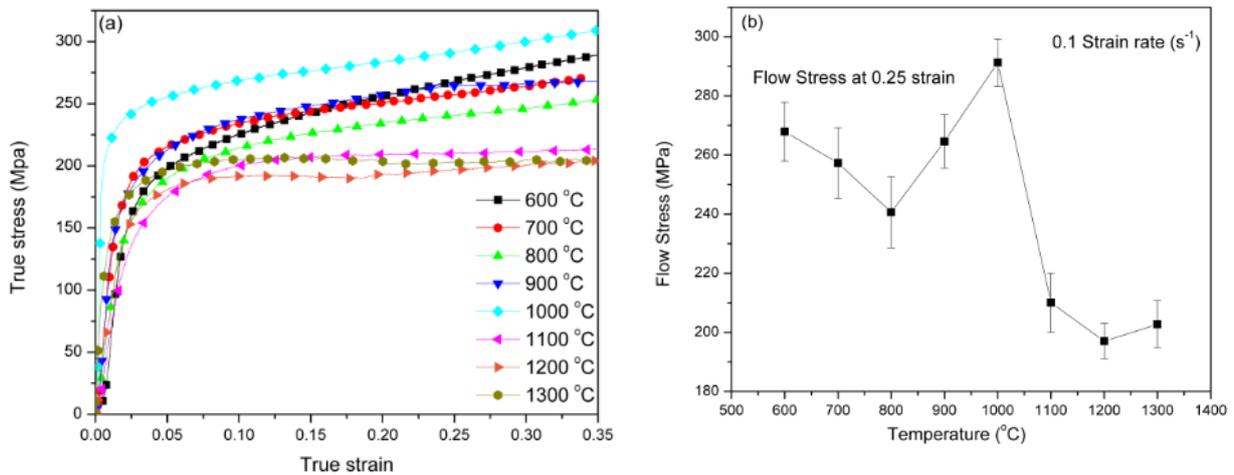


Fig. 4. Compression (a) stress-strain curve and (b) flow stress as a function of temperature for as-solidified Nb alloy from 600 C to 1300 C at 0.1 s^{-1} strain rate.

The second problem of profuse oxidation of Nb based alloys at temperatures above 800 °C was achieved by jacketing the material with copper. However, 800°C is just a warm temperature for the alloy and its strain rate sensitivity is very low at this temperature range, which indicates that the material has chances of failure during direct extrusion. Therefore, to avoid any chance of cracking of the material during working, a bore was drilled on each ingot and at 800 °C extrusion of hollow ingot was carried out with the help of a mandrel. This warm deformation imparted sufficient amount of strain in the alloy which eventually helped in bringing down the annealing temperature of the alloy to 1300°C. The optimized recrystallization parameters when implemented on the large size tubes it resulted in a grain size of $28 \pm 3 \mu\text{m}$ (Fig.5) [5].

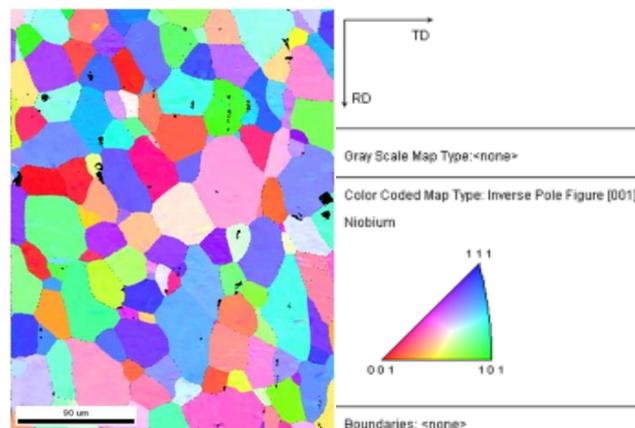


Fig 5: OIM micrograph of extruded Nb-1%Zr-0.1%C alloy annealed at 1300 °C for 3 hrs.

Based on the experimental studies on the effect of thermo-mechanical treatment on microstructure and properties of the Nb alloy, new flow-sheet for the low temperature fabrication of tubular products of Nb alloy has been developed and it has been successfully implemented on bulk scale to produce the Nb alloy tubular product as shown in Fig.6.

CHTR is being designed to operate at high temperatures (~1000 °C) using liquid metal (Pb-Bi) as coolant. In the absence of any data on thermal hydraulics and performance of structural materials which can sustain these temperatures, realistic designing of reactors is severely hampered. So far, all design parameters are based either on literature survey or extrapolated from the low temperature data. It is necessary to generate robust set of data on thermal hydraulics of the metal liquid phase. For this purpose, it is necessary to fabricate a test loop which can be operated around 1000°C. A high temperature liquid metal loop- named as *Kilo Temperature Loop* (KTL)-was decided to fabricate. As conventional materials like steel or superalloys, cannot be used at such high temperature, the Nb based alloy, Nb-1Zr-0.1C has been chosen to be the material for the loop component. The flow sheet developed for the fabrication of Nb tubes been successfully used for fabricating the Kilo Temperature Loop in collaboration with Nuclear Fuel Complex Hyderabad. The loop has been successfully tested at 1000 °C in Pb-Bi eutectic alloy environment [6].



Fig 6: Tubular product of Nb alloy obtained using low temperature deformation flow sheet.

Characterization of carbides in Nb alloy at different processing condition

Various morphologies of carbide precipitates observed in the as-solidified, deformed and annealed samples of the Nb alloy were characterized in detailed using Synchrotron X-ray diffraction (XRD), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) techniques [7]. Detailed analyses of synchrotron XRD and SAED (selected area electron diffraction) patterns obtained from the needle morphology (Fig.8) present in the as-solidified samples showed that precipitates are γ -Nb₂C carbide phase. Detailed analyses of high-resolution images of the phase showed the presence of coherent interface between the matrix Nb and Nb₂C carbide phases [7]. Based on these observations

formation mechanism for the Nb₂C phase was established which shows very small movement of Nb atoms and rearrangement of interstitial C atoms play a key role in the formation of the Nb₂C phase. Similarly, other carbides (needle and cuboidal morphology) present in the extruded samples were characterized by XRD and TEM (Fig.8). Based on their structural relationships it was shown that the as-solidified sample dissolved during deformation and re-precipitated in the form of (Nb,Zr)₂C and (Nb,Zr)₃C₂. As a result the sequence of phase transformation was established as: Nb₂C → (Nb,Zr)₂C + (Nb,Zr)₃C₂ → (Nb,Zr)C [7,8].

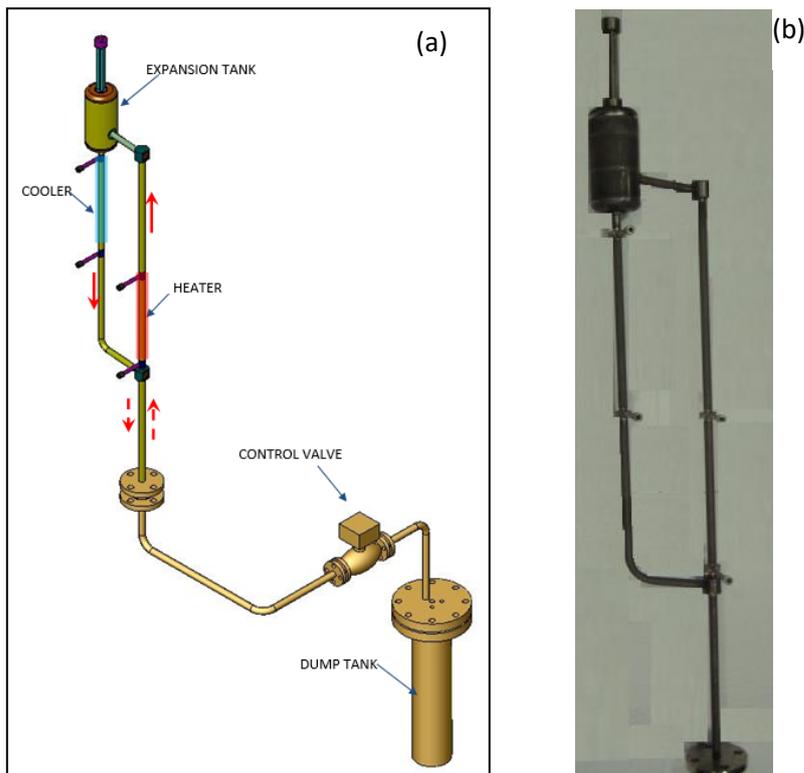


Fig. 7 (a) Isometric view of KTL (b) Kilo temperature loop fabricated with Nb alloy

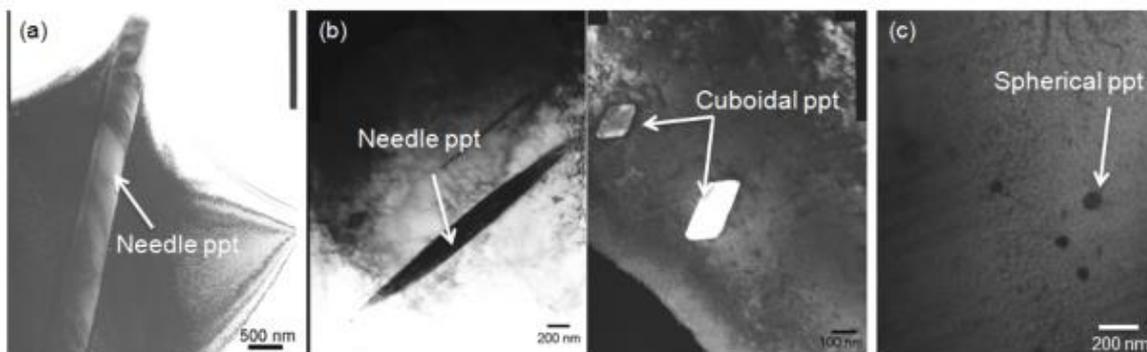


Fig:8 TEM micrographs of the (a) as-solidified (b) deformed and (c) annealed samples showing the presence of needle morphology, cuboidal and needle morphology, and spherical morphology carbide precipitates, respectively.

Nb Based In-situ Composites: A new approach for high temperature applications

In modern high-pressure turbines, higher entry temperature of ~1600 °C is achieved by the use of single crystals containing large concentrations of refractory metals for strengthening, and platinum group metals for topologically close-packed phase for better oxidation resistance and environmental coating that allow substrate surface temperatures to confine up to 1150°C. It is now very unlikely that Ni-based superalloys could be used in the hottest parts of 'future' engines as they would fail to meet the stringent environmental conditions imposed by regulatory organisations. Therefore, Nb silicide-based in-situ composites are being considered for their potential applications as next-generation turbine blade materials which can operate at temperatures which are significantly higher than the current superalloys-based materials. The word 'in-situ' was coined due to the fact that at elevated temperatures (during solidifications) silicides remains in the solution but once precipitate out it remains as second phase distributed in the Nb matrix nearly upto the vicinity of solidus temperature of the alloy. The presence of the silicide phase in the Nb matrix provides strength to the otherwise extremely soft Nb matrix at elevated temperatures. Besides, at low temperatures the matrix of Nb provides sufficient toughness to the brittle intermetallic phases. In addition, Nb matrix has serious limitation in terms of high temperature oxidation resistance which is significantly improved by the silicide phase. Therefore, symbiotic relationship between these phases makes this class of material very attractive for high temperature applications.

In the binary Nb-Si phase diagram, two phase field (Nb + Nb₅Si₃) is the most useful composition range where poor oxidation resistance, essentially because of the oxidation of the Nb matrix, could be improved by alloying with suitable elements like Ti, Hf, Cr, Al, B, to achieve a balance of high creep resistance, good oxidation resistance, and appropriate room-temperature fracture toughness. These alloying additions induces other phases in the alloy.. Among them the most important one is the Lave phase. These phases, likes Laves and Silicides, improve the oxidation resistance of Nb based in-situ composite materials. Typical microstructure of the in-situ composites consists of uniform distribution of silicides and Laves phases in ductile Nb solid solution (Nbss) matrix (Fig.9). It has been generally observed that those elements, like Ti, which improve oxidation of the alloy, deteriorate its high temperature strength. Therefore, selection of right set of elements and their concentration in the alloy are important. Fig. 10 provides a comparison of effect of different alloying elements on the oxidation response of various Nb-Si based alloys. For the purpose of

comparison Superalloys and Mo based alloys are also added in the figure. Detailed study on various alloying elements have been carried out [9,10]. Table 2 provides a list of alloying elements used in the study of the development of in-situ composites in DAE.

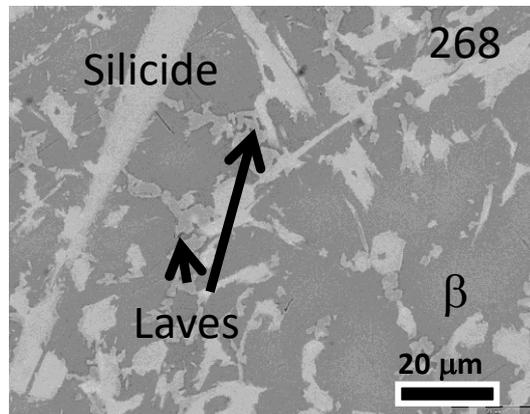


Fig. 9 Typical distribution of phase in in-situ Nb composites [9]

Between the alloy 266 with W and alloy 268 without W, immediate effect of W could be realized. From figure 11 it can be seen that W has significantly refined the microstructure. Similarly, comparison between the microstructures of 266 and 2404 clearly shows that upon reducing Cr concentration below 7%, formation of Laves phase was suppressed. Absence of the Laves phase has significantly reduced the oxidation properties of the alloy. Upon increasing Cr above 7% and adding Zr,Hf and Mo (2534) or adding Fe,B, W, Sn, oxidation properties could be restored.

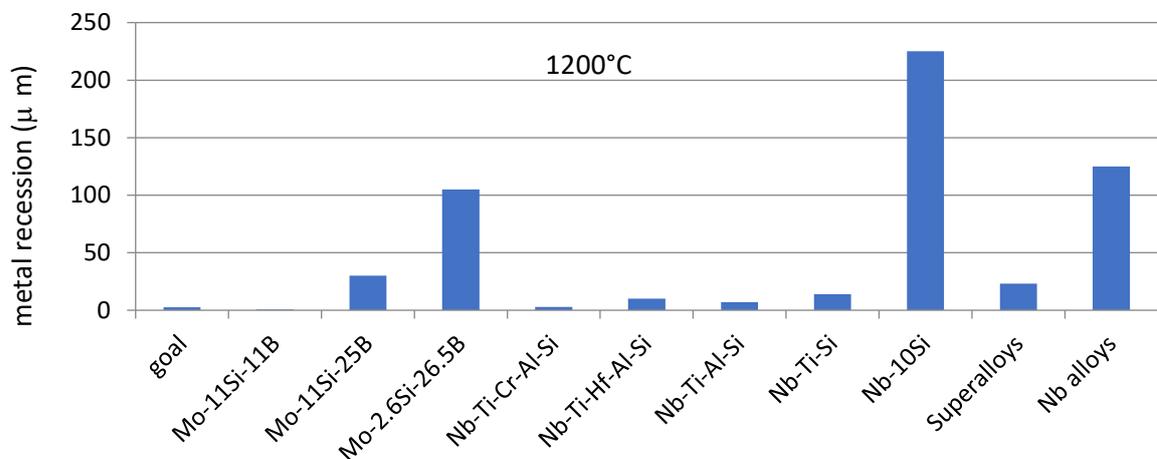


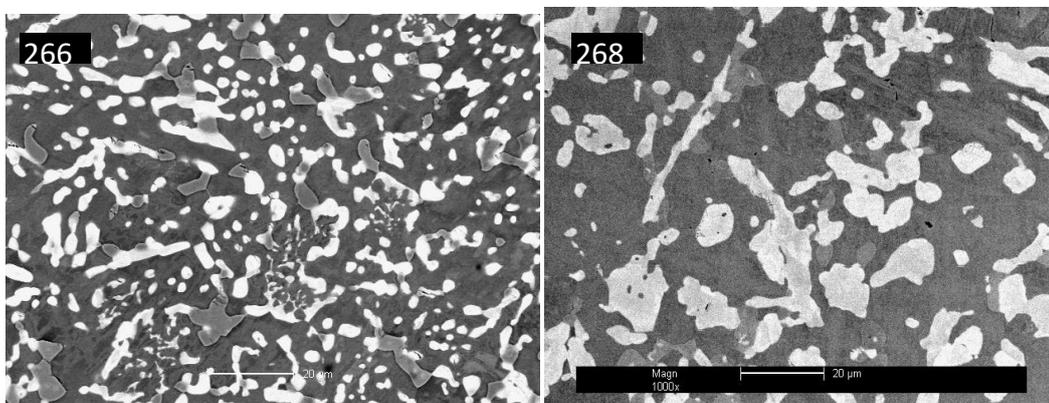
Fig. 10 A comparison of the properties of various in-situ composite alloys.

Table 2 *Composition of various alloys*

Alloy	Composition (at %)											
	Nb	Ti	Si	Al	Cr	Zr	Hf	Sn	W	Fe	B	Mo
266	33.9	29.05	7.73	10.06	10.18	3.65	3.08	1.32	1.03			
267	33.62	29.38	8.39	9.98	9.97	3.4	3.02	1.0	1.25			
268	33.42	29.48	7.86	10.17	10.42	4.03	3.71	0.9				
269	33.9	28.9	8.33	10.16	10.29	3.74	3.56	1.12				
2402	41.25	30.02	10.01	10.06	6.96	--	--	--	1.49			
2403	36.28	35.11	10.00	9.95	6.96	--	--	--	1.49			
2404	46.32	25.01	10.01	10.00	6.95	--	--	--	1.5			
R2505	31.99	35.01	12.0	10.0	7.0	--	--	1.0	1.0	1.0	1.0	
R2506	26.99	35.01	12.0	10.0	5.0	3.0	3.0	1.0	1.0	1.0	1.0	
R2534	32.65	12.76	14.28	10.20	7.66	5.10	5.10	--	--	---	2.04	10.21
R2535	32.04	35.01	9.00	10.00	9.0	---	---	1.5	1.5	1.0	0.7	

Based on detailed study comprising various configuration of elements it was observed that:

- (i) Addition of Ti beyond 35% in the alloy induces tendencies of phase separation.
- (ii) Al could be a good alloying element but if its concentration increases more than 7%, formation of Nb₃Al phase significantly reduces the room temperature ductility of the alloy.
- (iii) Minimum 7% Cr is needed for improving the oxidation of the alloy.
- (iv) Hf and Zr should be as low as possible.
- (v) Fe, B and Sn have positive effect on the oxidation properties of the alloy.
- (vi) Addition of small quantity of Mo improves the strength significantly.
- (vii) W addition refines the grain size but formation of WC precipitates is not noticed.



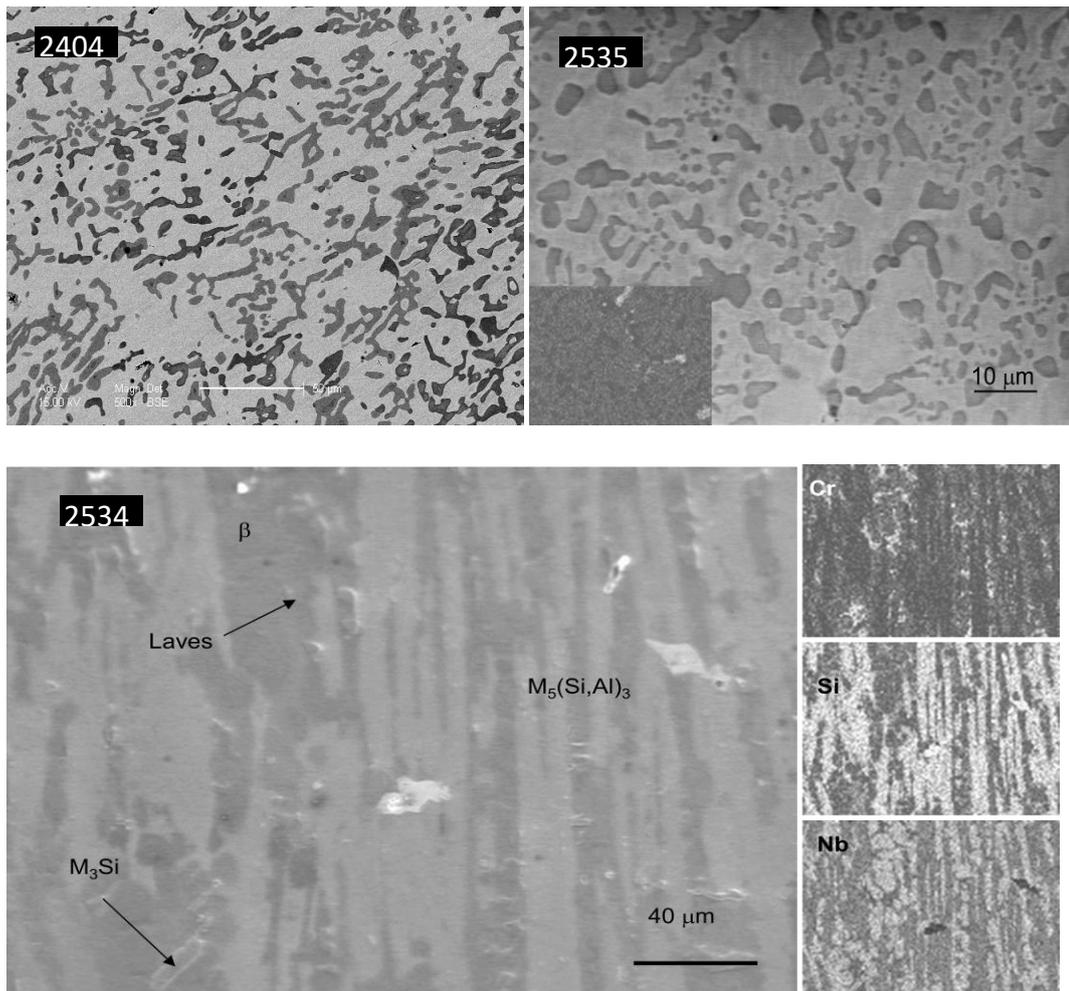


Fig. 11 Microstructures of various homogenized alloys listed in Table 2.

When the oxidation of these alloys were compared with those reported in literature, it was observed that these alloys offer better oxidation properties. In addition, low working temperature of 1300°C make these alloys amenable to good formability. Typical 0.2% YS of 275 MPa close to 1000°C make them an attractive choice for many structural applications [9,10].

Table 3 Comparison of various Nb based in-situ alloys

Alloy composition	Temperature °C	Time(h)	Oxidation weight gain(mg/cm ²)
Nb-8Si-11Al-15Ti	1000	100	120
CMSX 10 Ri	1177	100	88
PWA 1484	1177	100	26

41.2Nb-15.2Si-23Al-23Ti-4.7Hf-11.2Cr -4.7Ge(UES-AX)	900	100	-400
Nb-24Ti-16Si-6Al-6Cr-2Hf-(NbSi ₂ coatings)	1250	80	11.7
Nb-25Ti-13Si-2Al-3Cr-2Hf-0.3Sn-5Ge-3Fe	1000	60	~-48
Nb-25Ti-13Si-2Al-6Cr-2Hf-0.3Sn-5Ge	1000	100	-12
Alloys in the present study	981	100	8

Points to be noted

Nb based alloys have attractive properties for much wider applications. However, the cost of the Nb is one major deterrent for its usage for various applications. In spite of that a deep understanding of the Nb-based alloys in terms of oxidation properties, precipitation of various phases and their influence on high temperature properties has been carefully examined. Suitable environmental barrier coatings, to improve oxidation resistance could be another approach to address the high temperature oxidation issues.

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